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Effect of Trace Metals and Sulfite Oxidation of Adipic Acid Degradation in FGD Systems

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EFFECT OF TRACE METALS AND SULFITE OXIDATION ON ADIPIC ACID DEGRADATION IN FGD SYSTEMS

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Adipic Acid	Manganese	Stationary Sources	07C	
Degradation	Temperature	Trace Metals	14G	
Flue Gases	pH	Sulfite Oxidation	21B	
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SECTION 1

INTRODUCTION

The addition of adipic acid to flue gas desulfurization (FGD) wet scrubbers has been shown to benefit both SO_2 removal and limestone utilization. Adipic acid has the effect of buffering scrubber solutions, thereby improving liquid phase mass transfer. The use of adipic acid was first proposed by Rochelle (1) and has been tested by EPA in pilot systems at the Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina and at the TVA Shawnee Test Facility at Paducah, Kentucky.

Results from these test programs show that adipic acid is effective as a scrubber additive at concentrations in the range of 700-2000 ppm. However, overall mass balances on these pilot systems revealed that unaccounted-for losses of adipic acid were occurring. These losses were presumed to be the result of chemical degradation of adipic acid.

Further testing at the Shawnee test facility indicated that adipic acid degradation could be quenched by operating below pH 5.1. Since these unexpected but favorable results could be significant to the future application of adipic acid as a scrubber additive, independent verification was desired. Radian was contracted by EPA to conduct a systematic study of the effect of scrubber operating conditions on adipic acid degradation. The initial objectives of the study were to:

- Set up a bench-scale FGD system capable of closed-loop operation which could be used to simulate adipic acid degradation in full-scale FGD systems,
- Verify the quenching of adipic acid degradation at low pH observed at Shawnee, and

- Conduct parametric studies to more fully characterize the effects of key operating variables on adipic acid degradation.

The initial bench-scale runs were part of a parametric test series designed to evaluate the effects of pH, forced versus natural oxidation, and the adipic acid concentration. The results of these tests indicated substantial adipic acid degradation was occurring, even at pH values as low as 4.6. Prior to completing the parametric test series, however, the bench-scale unit was taken to the Shawnee Test Facility. A series of runs was performed there to determine if the zero-degradation results reported by Shawnee could be caused by a component in boiler flue gas or fly ash. Following this test series, the bench-scale unit was taken to the City Utilities Southwest Power Station in Springfield, MO. The purpose of these tests was to develop data which could be used to predict the adipic acid degradation rate for that system during full-scale performance testing. The predictive data was to be based on a comparison of the bench-scale degradation results from Springfield with those obtained at Shawnee and from prior laboratory testing.

Laboratory bench-scale degradation testing was resumed following the completion of field testing at Shawnee and Springfield. The program objectives, however, were altered somewhat in accordance with recent improvements in the understanding of the adipic acid degradation mechanism; most notably, the apparent effect of manganese ions on reducing the adipic acid degradation rate. An extensive data base for the effects of operating conditions and manganese on the adipic acid degradation rate was generated during this phase of testing.

During the latter phase of laboratory bench-scale testing, major emphasis was placed on the development of analytical techniques for the identification and quantification of adipic acid degradation products. Gas chromatography (GC), ion chromatography (IC), and ion chromatography-exclusion (ICE) techniques were developed to measure adipic acid degradation products in both the scrubber slurry and flue gas streams.

The major results obtained from the bench-scale testing experiments and the investigation of degradation products are given in Section 2 of this report. Conclusions and recommendations based on these results are also included in this section.

Section 3 contains a detailed discussion of the results of bench-scale adipic acid degradation testing. Topics presented here include a description of the bench-scale system, data from individual bench-scale system runs, and a discussion of the effects of various operating conditions on adipic acid degradation. The operating conditions discussed in this section include the rate of sulfite absorption/oxidation, pH, hold tank temperature, adipic acid concentration, sulfite ion concentration, thiosulfate, limestone, fly ash, and the effects of trace metals including manganese and iron.

During early bench-scale system testing, it was found that adipic acid was removed from the system through coprecipitation or occlusion in the scrubber solids. Under natural oxidation conditions, this mechanism of adipic acid loss can be a significant fraction of total adipic acid losses. The results of bench-scale testing and additional laboratory testing related to this phenomena are discussed in Section 4.

Analytical procedures have been developed for identification and quantification of adipic acid and its degradation products in both liquid and gas phase samples. These techniques are described in Section 5. This section also includes the results of analyses for adipic acid degradation products performed on numerous liquid and gas phase bench-scale samples.

Additional laboratory experiments were performed to provide clarification of unusual results observed during bench-scale testing:

- A laboratory program was initiated to determine the cause of continuing decomposition of adipic acid in samples from the bench-scale runs performed at Springfield.

- Scanning electron microscopy (SEM) was used to examine the crystal morphology and size of a variety of solids samples to determine if adipic acid has an effect on solids precipitation.

- Multiple analyses were performed on a filtrate sample obtained from the Shawnee pilot plant. This sample was of considerable interest because it contained large concentrations of the so-called Shawnee mystery peak.

The results of these experiments are given in Section 6.

Routine analytical techniques used during bench-scale testing are described in Appendix A. The analytical techniques described here are those not involving the measurement of adipic acid or its degradation products. This section also contains a summary of QA/QC procedures for the measurements and analyses performed during this program.

A sample calculation showing the methods used to obtain the adipic acid degradation rate from the raw data is given in Appendix B. A discussion of the experimental uncertainty associated with the bench-scale results is also given here.

SECTION 2

SUMMARY OF RESULTS AND CONCLUSIONS

An experimental study of the effects of scrubber operating variables on adipic acid degradation has been conducted for the Environmental Protection Agency (EPA) by Radian Corporation. This investigation involved two distinct areas of experimentation. The first was a study of the effects of scrubber operating variables on the adipic acid degradation rate. The adipic acid degradation experiments were performed using a bench-scale flue gas desulfurization (FGD) unit which was designed to simulate many of the important characteristics of full-scale FGD systems.

Secondly, in conjunction with the bench-scale testing, analytical procedures were developed for the identification and quantification of the adipic acid degradation products. These techniques were used to analyze many of the samples produced during bench-scale testing. Samples obtained from pilot-plant operation with adipic acid at TVA's Shawnee test facility at Paducah, KY, and from the full-scale adipic acid demonstration program at the City Utilities Southwest Power Station in Springfield, MO, were also analyzed for adipic acid and its degradation products.

2.1 RESULTS OF THE BENCH-SCALE ADIPIC ACID DEGRADATION TESTING PROGRAM

A bench-scale FGD unit was constructed to determine the effects of operating variables on the adipic acid degradation rate. The following variables were investigated:

- SO_2 absorption/oxidation rate,
- Adipic acid concentration,
- pH,
- Trace metals (manganese, iron),

- Limestone and limestone + fly ash (versus reagent grade $CaCO_3$),
- Boiler flue gas (versus synthetic flue gas),
- Temperature,
- Thiosulfate (as an additive), and
- Sulfite concentration.

The effects of each of these variables on the adipic acid degradation rate are summarized in the following subsections.

2.1.1 Results of Baseline Adipic Acid Degradation Testing

A total of 43 bench-scale runs were performed. Twenty-one of these runs were baseline tests in which the variables under consideration were limited to the SO_2 absorption/oxidation rate, the adipic acid concentration, and pH. $CaCO_3$ was used as the alkaline species for all baseline tests. The ranges for the variables investigated in the baseline tests were:

Variable	Range
SO_2 absorption rate	2.07 - 7.86 g SO_2/hr
Percent solids oxidation (a measure of the total absorbed SO_2 that is oxidized to sulfate)	9.7 - 100%
Adipic acid concentration	876 - 10080 ppm
pH	4.6 - 5.5

The resulting adipic acid degradation rates ranged from 15.4 to 600 mg/hr. A computer program was used to perform a statistical analysis on the baseline test data. This analysis showed that the adipic acid degradation rate was a function of the overall SO_2 oxidation rate and the adipic acid concentration. The degradation rate was found not to depend on pH, at least over the range tested. The sulfite ion concentration was also included in this analysis. However, the sulfite concentration was generally a function of pH and was also found not to influence the adipic acid degradation rate. A weighted least squares analysis was used to correlate the significant variables. The resulting correlation, which represents the best fit of the experimental data, is given below (for data at 50°C):

$$\begin{array}{l}\text{adipic acid}\\ \text{degradation rate,}\end{array}\ \text{mg/g } SO_2 \text{ removed} = 0.00308 \left(\begin{array}{c}\text{adipic acid}\\ \text{concentration, ppm}\end{array}\right)^{0.5542} \left(\text{percent oxidation}\right)^{1.185}$$

(correlation coefficient, $r^2 = 0.96$)

This correlation indicates that the adipic acid degradation rate, normalized by the SO_2 removal rate, is roughly proportional to the percent oxidation of the solids times the square root of the adipic acid concentration. A graph of the above correlation is shown in Figure 2-1.

2.1.2 Effect of Manganese on the Adipic Acid Degradation Rate

Several runs were performed with manganese, manganese plus iron, Springfield limestone, and Springfield limestone plus fly ash. The common factor involved in all these runs was the presence of manganese ions in the scrubber liquor. The resulting concentrations of manganese ranged from 2 to 21 ppm. The presence of manganese caused a significant reduction in the adipic acid degradation rate. Reductions of 42.5 to 85.4 percent below the adipic acid degradation rates predicted from the baseline correlation were observed for forced oxidation runs.

The adipic acid degradation rate was found to be a function of pH when manganese ions were present. The results show that a decrease in pH is accompanied by a decrease in the adipic acid degradation rate. In the baseline runs, in which no manganese was present, no pH effect was observed. At a given pH, the degradation rate also appears to be a function of the manganese concentration. The data supporting this result, however, are somewhat limited.

Several forced oxidation runs were performed in which Springfield limestone, rather than $CaCO_3$, was used as the source of alkalinity. The adipic acid degradation rates seen in the limestone tests were significantly below

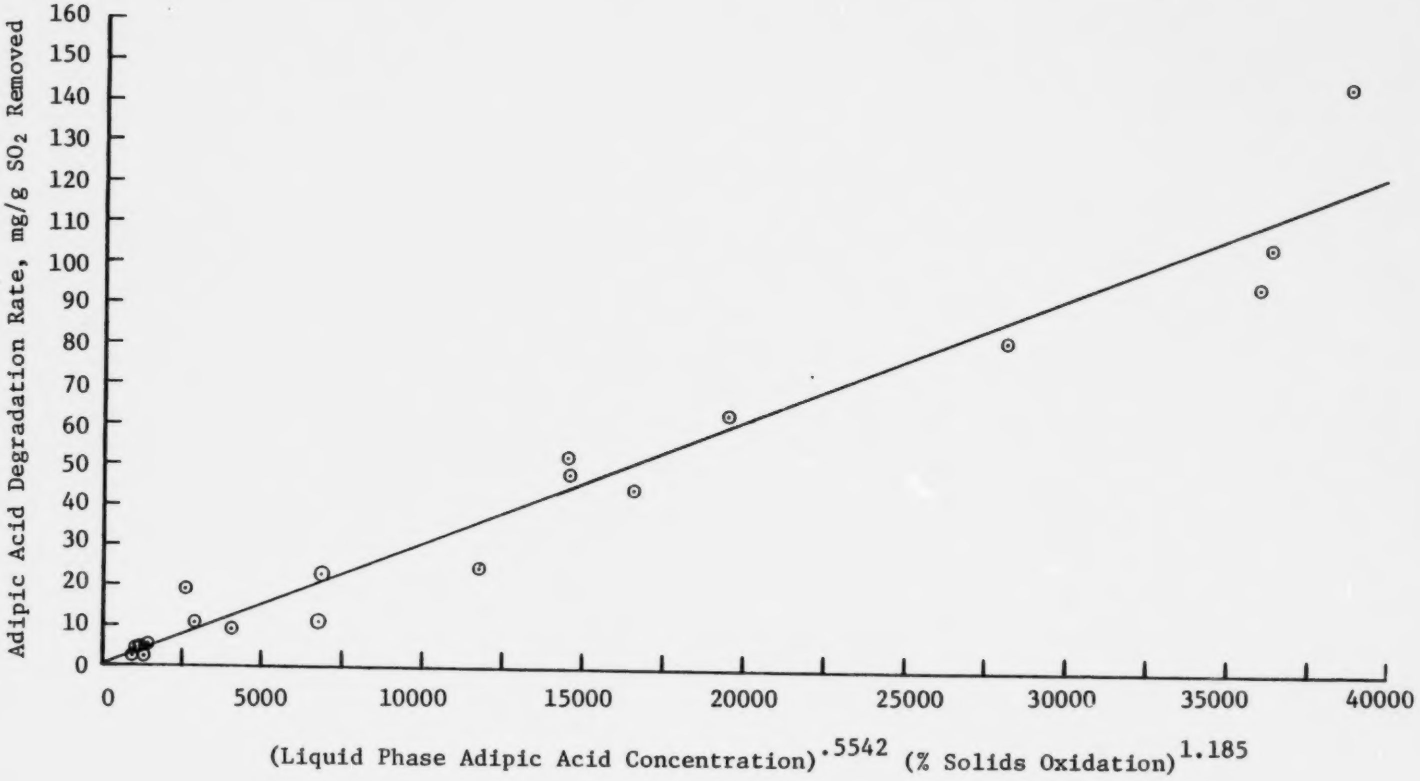

Figure 2-1. Correlated relationship between the adipic acid degradation rate, the liquid phase adipic acid concentration, and the percent solids oxidation for the baseline data set.

those seen in similar baseline tests with $CaCO_3$. This limestone was analyzed for trace metals and a significant quantity of manganese was found. Some of this manganese dissolved in the scrubber liquor during the bench-scale tests. The resulting adipic acid degradation rates were about the same as those seen in runs with $CaCO_3$ in which manganese was added to the hold tank.

The combination of limestone and fly ash was also tested. The resulting acipic acid degradation rate did not differ significantly from that of limestone alone. In bench-scale tests at Shawnee and Springfield, in which boiler flue gas with fly ash was utilized, no significant effect of fly ash was observed. A separate run, evaluating the effect of fly ash alone, was not performed.

Several forced oxidation tests with both manganese and iron were attempted. However, iron was found to be essentially insoluble and only small concentrations of iron (<2 ppm) could be held in solution. Again, the resulting adipic acid degradation rates were about as expected, based on the pH and the concentration of manganese in the hold tank.

A natural oxidation run with manganese was also performed. However, under natural oxidation conditions, only a small amount of the added manganese remained in solution (2 ppm) and the resulting adipic acid degradation rate was actually above that predicted from the baseline correlation.

The concentration of manganese which could be held in solution was found to vary with both pH and the level of oxidation. Generally speaking, more dissolved manganese was observed when operating under forced oxidation conditions than under natural oxidation conditions. At a given level of oxidation, the concentration of dissolved manganese increased with decreasing pH. A survey of the available literature indicates that manganese can remain in solution only in the +2 oxidation state. Further, Mn^{+2} is probably not oxidized to the +4 or +7 oxidation states in scrubber solutions (2)(3). Since less manganese could be held in solution during natural oxidation tests, the precipitate is most likely $MnSO_3$. This possibility, however, was not verified by analysis.

The above results regarding the effects of manganese on the adipic acid degradation rate are illustrated in Figure 2-2. This diagram shows a plot of the adipic acid degradation rate constant, K_d, versus pH. The rate constant K_d used here is simply the adipic acid degradation rate normalized by the total sulfite oxidation rate and the average adipic acid concentration. K_d is a convenient method of comparing the results of runs at different adipic acid concentrations and levels of oxidation. The value of K_d for the baseline runs without manganese ranged from 1.24 to 1.62 for the range of variables shown in Figure 2-2. The reduction in degradation due to manganese is evident in Figure 2-2 as the values observed for K_d range from 0.2 to 0.93. The results shown in Figure 2-2 also illustrate the dramatic effect of pH on the adipic acid degradation rate in the presence of manganese.

2.1.3 Results of Bench-Scale Testing at Shawnee and Springfield

A series of bench-scale tests using boiler flue gas was conducted at TVA's Shawnee FGD test facility at Paducah, KY and at City Utilities Southwest Power Station in Springfield, MO.

Three natural oxidation runs using $CaCO_3$ were performed at Shawnee. The adipic acid degradation rates seen in these runs were not significantly different from that predicted from the baseline correlation. This result indicates that the fly ash in the Shawnee flue gas had no effect on the adipic acid degradation rate under natural oxidation conditions. Manganese from fly ash may accumulate under forced oxidation conditions and result in decreased adipic acid degradation. This possibility, however, was not evaluated in these tests.

Four natural oxidation tests using limestone were performed at Springfield. In one of these tests, manganese was added to the hold tank. The

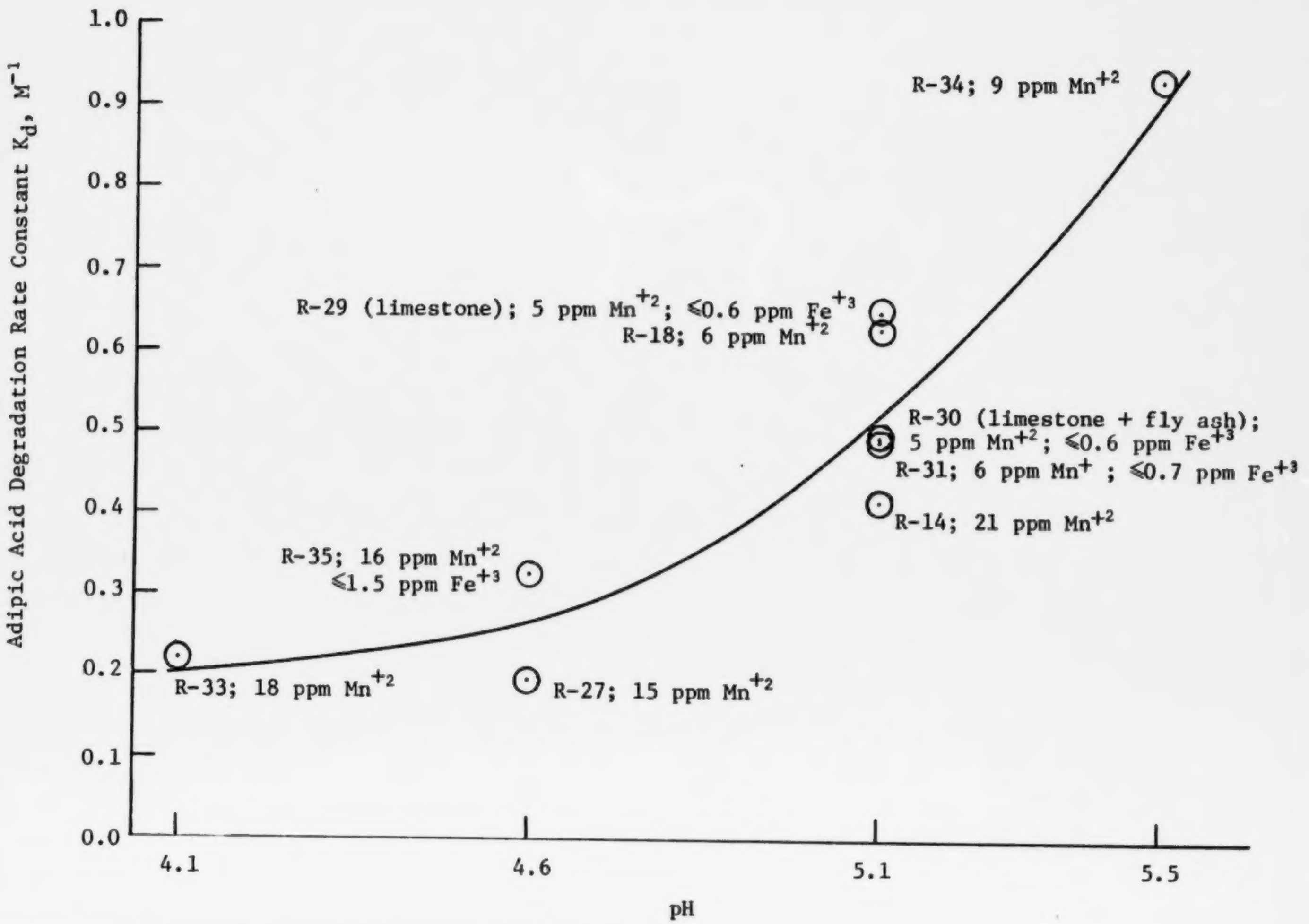

Figure 2-2. Effect of pH on the adipic acid degradation rate constant K_d for forced oxidation runs with manganese, manganese + iron, limestone, and limestone + fly ash. (Adipic acid concentrations for these runs varied from 1820 to 3310 ppm.)

degradation rates for the three tests with limestone only were not significantly different than that predicted from the baseline correlation. This result conflicts with the results of forced oxidation tests with limestone in which substantial reductions in the degradation rate were observed. However, in contrast to the forced oxidation runs, almost none of the manganese in the limestone dissolved under natural oxidation conditions. A comparison of these results again illustrates what may be an important effect related to the use of limestone. Specifically, the concentration of manganese which can be held in solution appears to be greater under forced oxidation conditions than under natural oxidation conditions. Stated in a slightly different manner, the increase in the adipic acid degradation rate resulting from an increase in the rate of sulfite oxidation may be offset somewhat by higher levels of dissolved manganese when limestone containing manganese is used.

As stated above, manganese was added to the hold tank in one of the natural oxidation runs at Springfield. In this test, excess manganese was added and some of the manganese (≃13 ppm) remained in solution. The resulting adipic acid degradation rate was 59 percent below that predicted by the baseline correlation. This indicates that manganese is also effective in reducing the adipic acid degradation rate under natural oxidation conditions if sufficient quantities of manganese can be held in solution.

2.1.4 Effect of Temperature on the Adipic Acid Degradation Rate

Three similar runs were performed in which the temperature of the hold tank was varied from 93 to 146°F. The results of these runs showed that the adipic acid degradation rate increased with increasing temperature. The effect of temperature on the rate of a chemical reaction can often be modeled by the following empirical equation (4):

$$K = A \exp\{-E_a/RT\}$$

where,

K = the chemical rate constant or an equivalent expression for the reaction rate, A = a pre-exponential constant,

E_a = the Arrhenius activation energy,

R = the ideal gas constant, and

T = the absolute temperature.

From the bench-scale data, the Arrhenius activation energy was determined to be 10.6 Kcals/mole. This value is typical of organic reactions in which the rate is controlled by a chemical reaction rather than a physical process such as diffusion.

When considering the effect of temperature on the adipic acid degradation rate, it is implied that the temperature of interest is the temperature at which sulfite oxidation is occurring. In forced oxidation systems, the majority of the sulfite oxidation takes place in the hold tank and the hold tank temperature, along with other factors, will determine the degradation rate. In natural oxidation systems, however, sulfite oxidation takes place in the scrubber, therefore, the temperature of interest is the temperature within the scrubber. This is important as the temperature within the scrubber may be somewhat higher than that of the hold tank.

2.1.5 Effect of Sulfite Ion Concentration and Thiosulfate

In the analysis of the baseline test results, the sulfite ion concentration was not found to have an effect on the adipic acid degradation rate. However, in these tests, the equilibrium sulfite ion concentration was a strong function of pH. To obtain an independent determination of the effect of the sulfite ion concentration, the sulfite concentration was increased from 470 to 2600 ppm via the addition of sodium ions (as Na_2SO_4). In this way, the effect of different sulfite ion concentrations could be evaluated at the same pH. A comparison of the degradation rates from these tests with the values predicted from the baseline correlation indicates that the sulfite ion concentration has little, if any, impact on the adipic acid degradation rate.

An increase in the sulfite concentration did result in a substantial increase in the percent solids oxidation over that typically seen in baseline natural oxidation runs. And, the increased level of oxidation did result in a higher absolute degradation rate. However, when this degradation rate is normalized with respect to the sulfite oxidation rate and the adipic acid concentration, the result is essentially equivalent to that predicted by the baseline correlation. This indicates that the sulfite concentration has no impact on the degradation mechanism.

2.1.6 Summary and Interpretation of the Effects of Important Operating Variables Influencing Adipic Acid Degradation

The variables found to have a significant impact on the adipic acid degradation rate are given below:

- The total sulfite oxidation rate (or equivalently, the product of the SO_2 removal rate and the mole fraction solids oxidation),
- The adipic acid concentration,
- pH (only if manganese is present),
- The manganese concentration in solution, and
- Temperature (hold tank temperature for forced oxidation systems and scrubber temperature for natural oxidation systems).

The most commonly proposed mechanism for adipic acid degradation suggests that the degradation rate is proportional to both the rate of sulfite oxidation and the adipic acid concentration, and is inversely proportional to the sulfite ion concentration (5)(6). The results of bench-scale testing tend to support the proposed proportionality between the degradation rate and the level of sulfite oxidation. The bench-scale data, however, suggests a less than linear dependence between the degradation rate and the adipic acid concentration. Accounting for this observation in terms of the proposed degradation rate mechanism is somewhat difficult. The half-order dependence of degradation on the adipic acid concentration may be the result of the high adipic acid concentrations (>10,000 ppm) used in some of the bench-scale tests or the result of some other variable not included in the correlation. In any event, the data clearly show that, from an operational standpoint, an increase in the adipic acid concentration does not result in a linear increase in the adipic acid degradation rate.

The proposed mechanism for adipic acid degradation also suggests that the degradation rate should be inversely proportional to the sulfite ion concentration. This effect cannot be substantiated by the bench-scale results. In the baseline tests, the sulfite ion concentration was allowed to float with pH. Analysis of this data showed no effect of sulfite or pH. In another test series, the sulfite ion concentration was changed at constant pH. In one such test, a fivefold increase in the sulfite ion concentration was obtained. The resulting degradation rate, however, was essentially equivalent to that predicted from the baseline correlation.

Manganese ions definitely cause a decrease in the adipic acid degradation rate. Manganese probably affects adipic acid degradation through a change in the mechanism of sulfite oxidation. Sulfite oxidation is thought to proceed through a free radical mechanism. Manganese may catalyze the sulfite oxidation reaction in such a way as to reduce the concentration of the free radical believed to be involved in adipic acid degradation. Alternatively, manganese may catalyze the sulfite oxidation reaction utilizing a mechanism which does not involve a free radical. The existence of at least two competing sulfite oxidation mechanisms, both of which could be functions of pH, might help in interpreting the dependence of the adipic acid degradation rate on pH when manganese is present.

Results obtained during adipic acid testing by EPA at the Shawnee test facility also show an effect of pH on adipic acid degradation (7). Their results show that degradation was reduced to zero below pH 5.1 under natural oxidation conditions when manganese was present. Although total quenching of adipic acid degradation was not achieved in the bench-scale tests, the results in Figure 2-2 do indicate that the degradation rate constant, K_d, is changing rapidly between pH 4.6 and 5.5.

The results of the bench-scale degradation tests with manganese have been used to estimate the expected degradation rates for forced oxidation tests at the full-scale adipic acid demonstration program in Springfield, MO. The adipic acid degradation rate for the full-scale system has been measured for three test periods. The results show degradation rates of 7.6 and 11.6 mg adipic acid degraded per g SO_2 absorbed (8). The bench-scale estimate of the degradation rate based on the operating conditions at Springfield, is 13.7 mg/g SO_2 removed.

Estimating the adipic acid degradation rate for a full-scale system from the bench-scale results is not entirely straightforward, particularly for natural oxidation systems. In a forced oxidation system, most of the sulfite oxidation takes place in the hold tank. Therefore, adipic acid degradation takes place at the conditions in the hold tank, i.e., the hold tank temperature and pH. In natural oxidation systems, however, sulfite oxidation takes place in the scrubber itself. In this case, the adipic acid degradation rate must be predicted based on the conditions which exist within the scrubber. Specifically, the temperature within the scrubber will be somewhat higher than the hold tank temperature and the pH in the scrubber will be somewhat lower than the pH in the hold tank. The complicated sulfite absorption/oxidation, pH, and temperature profiles within the scrubber make the estimation of the adipic acid degradation rate for full-scale natural oxidation systems somewhat more difficult.

2.2 RESULTS BASED ON ANALYSES OF SCRUBBER SOLIDS

Batch precipitation tests were performed in which calcium sulfite and sulfate solids were precipitated from solutions containing adipic acid. The results showed that large concentrations of adipic acid were either coprecipitated with or occluded in the calcium sulfite solids. By contrast, almost no adipic acid was found in calcium sulfate solids (gypsum). The results of these tests showed that the amount of coprecipitated or occluded adipic acid depends on the oxidation level and the liquid phase adipic acid concentration.

The results seen in the batch precipitation tests were also observed in the bench-scale solids analyses. The results of the bench-scale tests are illustrated in Figure 2-3 which shows a plot of the ratio of the solid and liquid phase adipic acid concentrations versus percent oxidation. Note that the solids adipic acid concentration used in Figure 2-3 refers to coprecipitated or occluded adipic acid only. That is, adipic acid in the liquid associated with the wet filter cake is not included. These results show that the adipic acid concentration in the solids is high at low oxidation levels and decreases to nearly zero at high oxidation levels.

Since the solids from the bench-scale system are produced under similar conditions as the solids in full-scale systems, the bench-scale results should be suitable for estimating adipic acid losses through coprecipitation or occlusion for full-scale systems. A limited amount of data was available from the full-scale Springfield demonstration program concerning coprecipitated or occluded adipic acid losses. These results are in reasonable agreement with the solid phase losses predicted in Figure 2-3.

Selected solids from the batch precipitation tests and the bench-scale tests were analyzed with a scanning electron microscope (SEM). The results of this analysis show that average size of calcium sulfite crystals decreased as the adipic acid concentration increased. The calcium sulfite crystal morphology also showed an increase in the aggregate structure with increasing concentrations of adipic acid. No change in crystal size or morphology was observed in gypsum crystals from forced oxidation runs at different adipic acid concentrations. This factor may result in a decrease in filter dewatering efficiency under natural oxidation conditions when adipic acid is present. No experiments were performed, however, to quantify this effect.

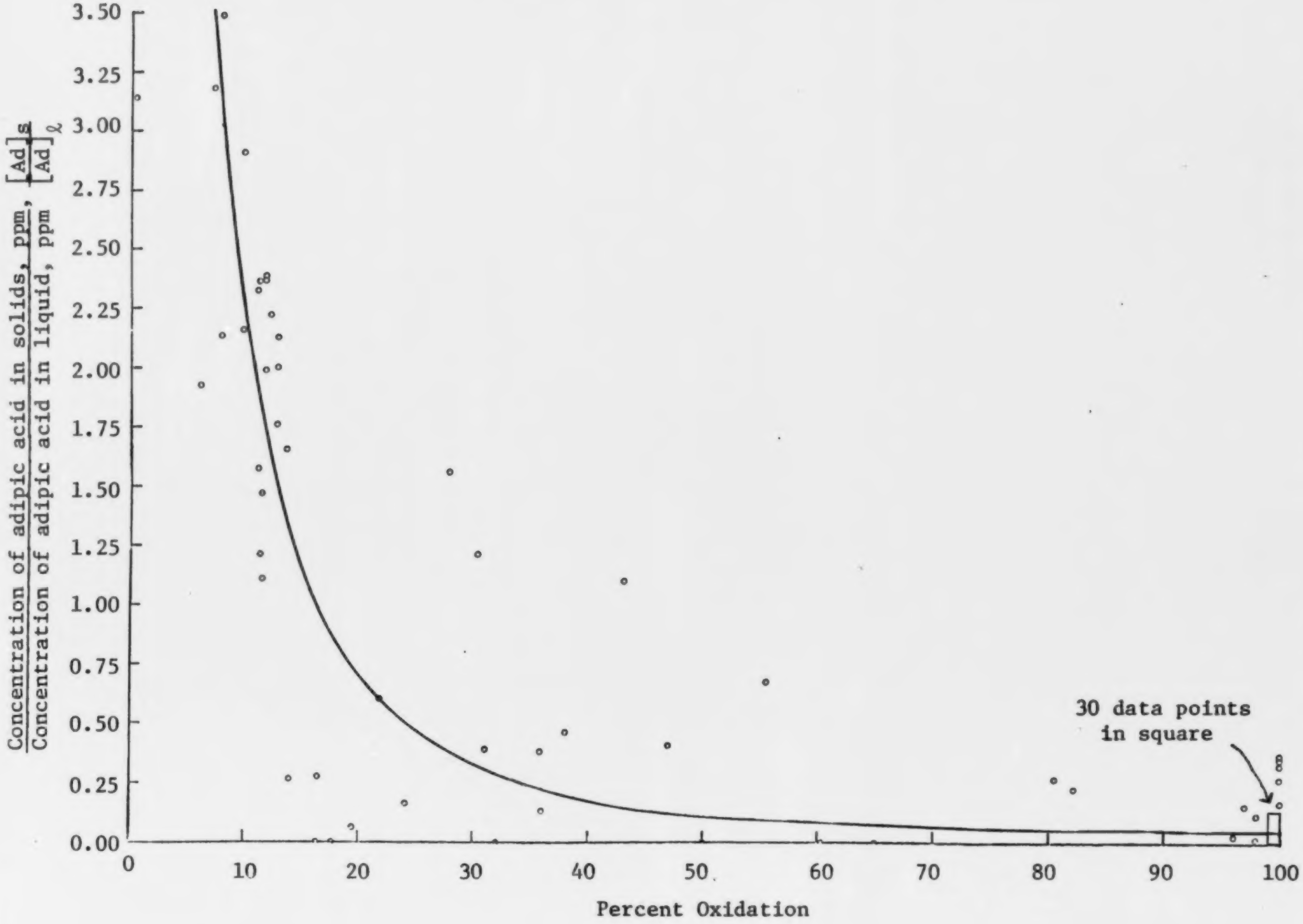

Figure 2-3. Relationship of adipic acid content of bench-scale solids to percent oxidation.

2.3 RESULTS OF THE ANALYTICAL DEVELOPMENT TASK

Three analytical techniques were used to identify and quantify the concentration of adipic acid and its degradation products. These techniques include:

- Ion chromatography (IC),
- Ion chromatography-exclusion (ICE), and
- Gas chromatography (GC).

The concentrations of liquid phase adipic acid, and liquid and solid phase chloride and sulfate were determined by IC. The IC technique is simple and yields reproducible results. Most of the adipic acid degradation products, however, cannot be determined by IC. In addition, glutaric acid coelutes with adipic acid which interferes with the determination of the adipic acid concentration.

The ICE technique was used to measure the concentrations of adipic acid in the scrubber solids and to determine the identity and concentration of some of the adipic acid degradation products. A hydrochloric acid dissolution was used to prepare solids for adipic acid analysis. The ICE technique utilizes an HCl eluent and the HCl used in the solids dissolution does not interfere with the analysis. The HCl makes analysis of the solids difficult by IC.

Gas chromatography (GC) techniques have been developed for the identification and quantification of adipic acid degradation products. These techniques include:

- Analysis of gas phase samples for hydrocarbons, and
- Analysis of liquid phase samples for both monoprotic and diprotic carboxylic acids.

Analyses for gas phase species were obtained by direct injection of the gas sample. The use of solid sorbents was avoided because problems such as variable trapping efficiency, incomplete desorption, and contamination are characteristic of solid sorbent techniques.

Liquid phase monoprotic carboxylic acids were analyzed by direct aqueous injection of the sample. Diprotic carboxylic acids could not be analyzed by direct injection because of their low volatility. The technique for diprotic carboxylic acids involved an ether extraction of the acids followed by methylation of the acid groups to form dimethyl esters. Both extraction efficiencies and methylation efficiencies were determined for each of the diprotic carboxylic acids.

The GC and ICE techniques were used to analyze for adipic acid degradation products in both gas and liquid phase bench-scale samples. Conclusions drawn from these analyses are given below:

- Valeric acid was identified in all but three samples, thereby lending support to conjugated oxidative decarboxylation as the degradation mechanism:

  $$\underset{\text{adipic acid}}{HO_2C(CH_2)_4CO_2H} \xrightarrow[\text{attack}]{\text{free radical}} \underset{\text{valeric acid}}{CH_3(CH_2)_3CO_2H} + CO_2$$

  It is also of interest to note that in virtually every case, butyric and propionic acids were only detected if valeric was also present. This lends credence to the stepwise process leading to progressively smaller products which is theorized to occur once valeric acid is formed (10).

- Large amounts of glutaric and succinic acid were formed in runs where manganese ions were present in the hold tank. Of the total amount of adipic acid degraded, from 13 to 41 percent could be accounted for as glutaric acid and up to 15 percent could be accounted for as succinic acid. In all other bench-scale runs, a maximum of 5 percent of the degraded adipic acid could be accounted for as glutaric acid. Apparently, the presence of manganese dramatically affects the degradation process by promoting the oxidative route and inhibiting the decarboxylative route. This, coupled with the preceding conclusion regarding the stepwise production of monocarboxylics, implies that adipic acid degrades by either a conjugated oxidative mechanism (i.e., adipic → glutaric → succinic → . . .) or a conjugated oxidative decarboxylation mechanism (i.e., adipic → valeric → butyric → . . .), and that there is little or no crossover between mechanisms once the process has begun.

- The analyses of liquid phase degradation products showed that from 14 to 75 percent of the degraded adipic acid could be accounted for in the liquid phase. This assumes that each molecule of adipic acid produced only one degradation produce molecule. In general, a higher percentage of the degraded adipic acid was recovered as degradation products in the forced oxidation tests than the natural oxidation tests (43% versus 29%).

- Analyses of gas phase hydrocarbons by GC showed significant concentration of ethane, propane and butane. Results from run R-24 showed roughly 57 percent of the degraded adipic acid could be accounted for by the observed concentration of hydrocarbons assuming that only one hydrocarbon molecule was formed from each degraded adipic acid molecule.

- Oxalic acid was not detected in any of the samples, therefore it either was not generated or it decomposed too rapidly to be seen. Since virtually every other carboxylic acid was detected, it appears that oxalic acid was produced but was unstable. Oxalic acid is known to readily decompose to CO_2.

- Acetic acid was only detected in three of the twenty-three samples, which tends to imply either an analytical error or an anomalous degradation mechanism. Since no attempt was made to confirm the presence of acetic acid by an independent method, it is difficult to assess the significance of the GC results.

A variety of analyses were performed on a filtrate sample obtained from TVA's Shawnee test facility. This sample was quite interesting because it contained an apparently large concentration of the so-called Shawnee mystery compound. The results of ICE and GC analyses, which are quite specific for adipic acid, showed that the actual concentration of adipic acid in this sample was about 530 ppm. The apparent concentration of adipic acid as determined by the silicic acid technique was nearly 1200 ppm. The difference between these determinations cannot be accounted for by the presence of identified degradation products. An investigation of the silicic acid technique indicated that this discrepancy is caused by the presence of large concentrations of Shawnee mystery compound.

At this time, the identity of the Shawnee mystery compound remains unknown. However, several clues regarding its identity have been determined.

These results are presented in Section 6.2 of this report to aid in any future effort to identify this material.

2.4 CONCLUSIONS AND RECOMMENDATIONS

The results contained in this report can be used to obtain a rough estimate of the adipic acid degradation rate and the total consumption rate of adipic acid for full-scale systems. An example of such an estimate is given in Figure 2-4. This figure shows the total consumption of adipic acid resulting from losses due to chemical degradation and losses in both the solid and liquid phases of the filter cake as a function of percent solids oxidation. The bases of this estimate are given below:

- The chemical adipic acid degradation rate constant, K_d, was assumed to be 0.5 M^{-1}. This is typical of the degradation expected at pH 5.1 for systems in which manganese is present at concentrations of about 20 ppm.
- The liquid phase adipic acid concentration was assumed to be 2000 ppm.
- The weight percent solids in the filter cake, from which the adipic acid loss in liquid associated with the filter cake is calculated, was assumed to be that determined during full-scale adipic acid testing at Springfield. Ten percent of the total solids were assumed to be inerts, either from the fly ash or the limestone.
- The loss of adipic acid coprecipitated or occluded in the waste solids was estimated from the bench-scale relationship illustrated in Figure 2-3.
- Closed loop operation was assumed. That is, no blow-down or miscellaneous slurry losses were considered.

The results given in Figure 2-4 show that each of the three major loss mechanisms can be responsible for the largest fraction of the total adipic acid loss, depending on the percent oxidation. At oxidation levels up to 15 percent, the largest loss of adipic acid is due to coprecipitation in the solids. From 15 to 30 percent oxidation, the loss of adipic acid in the liquid associated with the filter cake represents the largest loss. Above 30 percent oxidation, the chemical degradation of adipic acid predominates.

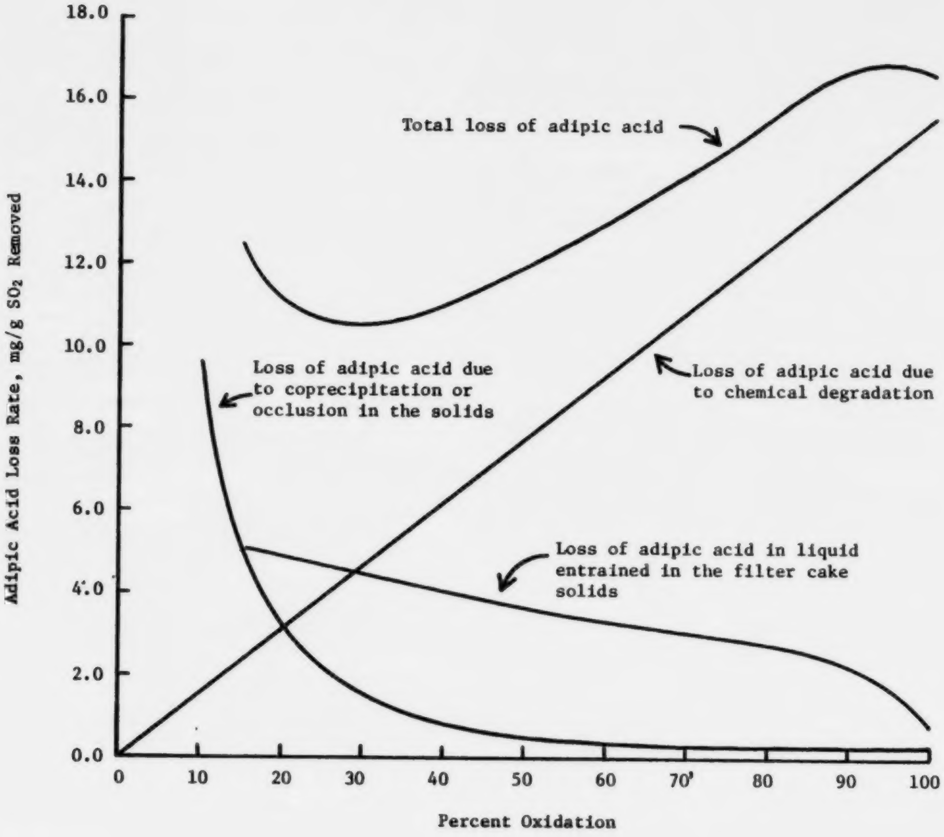

Figure 2-4. Estimated total adipic acid losses due to chemical degradation, coprecipitation or occlusion in the solids, and liquid entrained in the filter cake versus percent oxidation.

Also, the total loss function is seen to pass through a minimum at roughly 30 percent oxidation.

The above example is intended to illustrate the adipic acid loss profile for a typical full-scale FGD system. Naturally, this profile can change considerably depending on operating conditions and site-specific factors. In the above example, degradation losses were based on a value of $K_d = 0.5\ M^{-1}$. This is the predicted adipic acid degradation rate of pH 5.1 with 20 ppm manganese. If the pH was reduced to 4.6 for example, a lower chemical degradation rate would be expected and the total loss curve would become flatter and less dependent on percent oxidation. The opposite would be the case for operation at pH 5.5. Losses due to chemical degradation are also affected by the concentration of manganese, the hold tank temperature, and the adipic acid concentration.

Losses of adipic acid in liquid associated with the filter cake can also be expected to be site-specific due to differences in solids dewatering equipment. The percent solids achieved in the filter cake may also be affected by the concentration of adipic acid (see Section 6.3).

Losses of adipic acid through blowdown or spills were not considered in this example. In some FGD installations this loss mechanism may represent a large fraction of total adipic acid losses.

The results shown in Figure 2-4 show that adipic acid losses tend to increase at higher oxidation levels. During pilot testing at RTP and full-scale testing at Springfield, however, losses during forced oxidation were somewhat lower than those observed during natural oxidation tests (8)(9). There are three factors which were not incorporated into Figure 2-4 which help to explain this inconsistency:

1) Manganese concentrations higher than those evaluated in this program may be seen in full-scale systems,

2) Manganese is more soluble under forced oxidation conditions, and

3) Operation under forced oxidation conditions may result in higher concentrations of liquid phase degradation produces.

The basis for Figure 2-4 is an adipic acid degradation rate constant of 0.5 M^{-1} at 20 ppm Mn^{+2}. However, manganese concentrations of 60-70 ppm may be seen in actual FGD systems (7)(8). Therefore, the actual degradation rate constant at higher manganese concentrations is probably lower than 0.5 M^{-1}. However, insufficient data was obtained during this study to quantify the effects of manganese concentrations in excess of 25 ppm. Note that a reduction in the degradation rate constant from 0.5 to 0.2 M^{-1} results in roughly equivalent adipic acid losses at natural and forced oxidation.

The greater solubility of manganese under forced oxidation conditions must also be considered. In Figure 2-4, the assumption of a constant degradation rate constant results in a linear relationship between degradation losses and percent oxidation. In a full-scale system, with a particular limestone, fly ash, and flue gas, the concentration of manganese in the liquid phase will be higher under forced oxidation conditions. This will result in a decreasing degradation rate constant as percent oxidation increases. The slope, therefore, of the degradation losses in Figure 2-4 will decrease as percent oxidation increases. This factor tends to reduce forced oxidation losses relative to natural oxidation losses for the same FGD system.

Work performed during full-scale DBA (di-basic acid) testing at Springfield shows that succinic acid and glutaric acid coprecipitate in a manner similar to that of adipic acid under natural oxidation conditions. Further, the tendency to coprecipitate increases from adipic to glutaric to succinic acids (8). In fact, nearly all of the succinic acid component of the DBA mixture coprecipitated in the solids leaving almost no succinic acid in the liquid phase. It is likely that these dicarboxylic acid degradation products also show the tendency of adipic acid not to coprecipitate in gypsum (forced oxidation) solids. This hypothesis is supported by the observation that a higher percentage of the degraded adipic acid was recovered as liquid phase degradation products in the forced versus natural oxidation bench-scale runs. The above results are significant for several reasons:

- Succinic acid and glutaric acid are major adipic acid degradation products when manganese is present and should remain in solution under forced oxidation conditions,
- Succinic acid and glutaric acid enhance SO_2 removal in a similar manner as adipic acid. Therefore, a lower adipic acid concentration is required to achieve a given SO_2 removal efficiency. And, degradation of the adipic acid constituent is reduced to the extent that its concentration is reduced.

Although this effect does not reduce the adipic acid degradation rate constant, it will reduce the adipic acid addition rate necessary to achieve a given level of SO_2 removal under forced oxidation conditions. This may help to explain the reduced adipic acid consumption rate seen at forced versus natural oxidation.

The bench-scale results suggest that the following variables (in addition to the percent solids oxidation) can have an effect on the adipic acid degradation rate:

- The adipic acid concentration,
- pH (only if manganese is present)
- The manganese concentration in solution, and
- Temperature (hold tank temperature in forced oxidation systems and scrubber temperature in natural oxidation systems).

At a given type of operation (i.e., natural or forced oxidation) the minimum total loss of adipic acid must be determined by optimizing pH and the adipic acid concentration. Naturally, the optimization procedure must be performed within the constraints of the desired SO_2 removal efficiency. A result of the optimization procedure would be the equilibrium concentration of manganese. The use of additional manganese, however, is probably not a realistic option in a full-scale FGD system. A decrease in hold tank temperature in forced oxidation systems could result in enhanced SO_2 removal and decreased adipic acid degradation. However, flue gas temperatures in utility boilers are already minimized through the use of air preheaters and economizers. External cooling of the slurry may be possible. However, scaling problems and energy and equipment costs would make the design of such cooling systems impractical.

From the above discussion, it would appear that aside from the pH-adipic acid concentration optimization and, of course, minimizing miscellaneous slurry losses, there is little that can be done to reduce total losses of adipic acid. However, the bench-scale results do suggest that a change in the FGD system design may be useful in limiting total adipic acid consumption. One such design change is the use of two-tank forced oxidation. In this design, sulfite oxidation and limestone addition take place in separate tanks. The effluent from the scrubber is routed to the oxidation tank where sulfite oxidation occurs. The slurry from the oxidation tank is sent to the hold tank where limestone addition and gypsum precipitation occur. The advantage of this system over conventional single tank forced oxidation is that sulfite oxidation, and the resulting adipic acid degradation, take place at pH values below that of the hold tank. The resulting decrease in the total adipic acid consumption rate can be illustrated by comparing the estimated adipic acid consumption of a two-tank forced oxidation system with that of single-tank natural and forced oxidation systems. Data for the total loss rates of adipic acid from single tank forced and natural oxidation were given in Figure 2-4. The total adipic acid loss for the two-tank system can be estimated by assuming that the oxidation tank operates at 0.5 pH units below that of the hold tank. This would decrease the effective adipic acid degradation rate constant from roughly 0.5 to 0.2 M^{-1} at 20 ppm manganese (see Figure 2-2). Estimates comparing the total adipic acid consumption rate of a two-tank system with both natural and forced oxidation single-tank systems are given in Table 2-1. Again, miscellaneous slurry losses are not considered.

The results in Table 2-1 show that the total adipic acid consumption rate can be minimized using the two-tank forced oxidation design. This design may offer several other advantages as well:

TABLE 2-1. COMPARISON OF TOTAL ADIPIC ACID CONSUMPTION FOR A TWO-TANK FORCED OXIDATION DESIGN WITH CONVENTIONAL SINGLE-TANK NATURAL AND FORCED OXIDATION SYSTEMS

	Natural Oxidation System (40% Solids Oxidation)	Forced Oxidation (Single-Tank)	Forced Oxidation (Two-Tank)
Loss of adipic acid through chemical degradation, mg/g SO_2 removed	6.25	15.6	6.25
Loss of adipic acid through coprecipitation or occlusion in the scrubber solid, mg/g SO_2 removed	0.78	0.27	0.27
Loss of adipic acid in liquid associated with the filtered solids, mg/g SO_2 removed	4.02	0.75	0.75
Total adipic acid consumption, mg/g SO_2 removed	11.05	16.62	7.27

- Low pH in the oxidizer tank can promote sulfite oxidation (5) while high pH in the hold tank promotes SO_2 removal,
- The extra residence time provided by two tanks allows for more complete precipitation of calcium sulfate as well as improved limestone dissolution,
- The limestone blinding problem which is common in adipic acid enhanced forced oxidation systems can be minimized by oxidizing sulfite prior to limestone addition, and
- Gypsum solids from forced oxidation systems are easier to dispose of than solids from a natural oxidation system.

A disadvantage of the two-tank forced oxidation design is the necessity of two tanks. Economic factors will center on a trade-off between higher capital costs for the two tanks and lower operating costs due to a decrease in adipic acid consumption. A more detailed economic evaluation, however, is beyond the scope of this program. The two-tank forced oxidation design has been tested at TVA's Shawnee Test Facility and no serious operating problems were encountered (7).

SECTION 3

BENCH-SCALE SYSTEM ADIPIC ACID DEGRADATION TESTING

The results of bench-scale testing for determining the effects of operating conditions on adipic acid degradation are described in this section. The bench-scale test results were obtained during three phases of experimentation. The first phase consisted of laboratory testing at Radian. The second phase consisted of testing at the Shawnee test facility in Paducah, KY, and at the City Utilities of Springfield Southwest Power Station in Springfield, MO. The third phase consisted of additional laboratory testing at Radian.

The specific objectives of this study were to:

- Set up a bench-scale flue gas desulfurization (FGD) system capable of closed-loop operation which could be used to simulate adipic acid degradation in full-scale systems,
- Conduct tests to study the effect of key operating variables on the rate of adipic acid degradation, and
- Study the effect of trace metals, particularly manganese on the rate of adipic acid degradation.

A description of the bench-scale system is presented in Section 3.1. This section also describes the experimental procedure used to obtain adipic acid degradation rate data from the bench-scale scrubber.

A total of 43 runs were made using the bench-scale system. A description of each of these runs and a presentation of the resulting data base are given in Section 3.2. This information is given in a series of tables for reference during the remaining discussion of results. This section also contains a discussion of the various techniques that are used in this report to describe degradation rate data.

The effect of operating conditions on the adipic acid degradation rate is discussed in Section 3.3. Specific operating conditions are discussed in the following subsections:

- The effects of the rate of sulfite oxidation, the adipic acid concentration, and pH are discussed in Section 3.3.1.
- The effects of manganese and iron on the adipic acid degradation rate are discussed in Section 3.3.2. Effects relating to the use of Springfield limestone are also included in this section.
- The effects of boiler flue gas with fly ash from bench-scale testing at Shawnee and Springfield are discussed in Section 3.3.3.
- The effect of temperature on the adipic acid degradation rate is discussed in Section 3.3.4.
- The effects of sulfite concentration and the addition of thiosulfate are described in Section 3.3.5.

3.1 EXPERIMENTAL APPROACH

The design of the bench-scale system was influended by two important considerations.

- The desire to simulate the operation of full-scale FGD systems which would allow results from the bench-scale system to be used to estimate adipic acid degradation in larger systems, and
- The need for accurate mass balance determinations since certain sets of operating conditions were anticipated to produce low degradation rates.

The experimental equipment design which resulted from the above considerations is illustrated schematically in Figure 3-1. In general terms, the operation of the system consisted of contacting synthetic or boiler flue gas in a packed scrubber with recirculating slurry from the hold tank. The pH of the hold tank slurry was maintained at a constant level by addition of reagent grade $CaCO_3$ or limestone. Note that a bubbler contactor was used for Phase 3 testing.

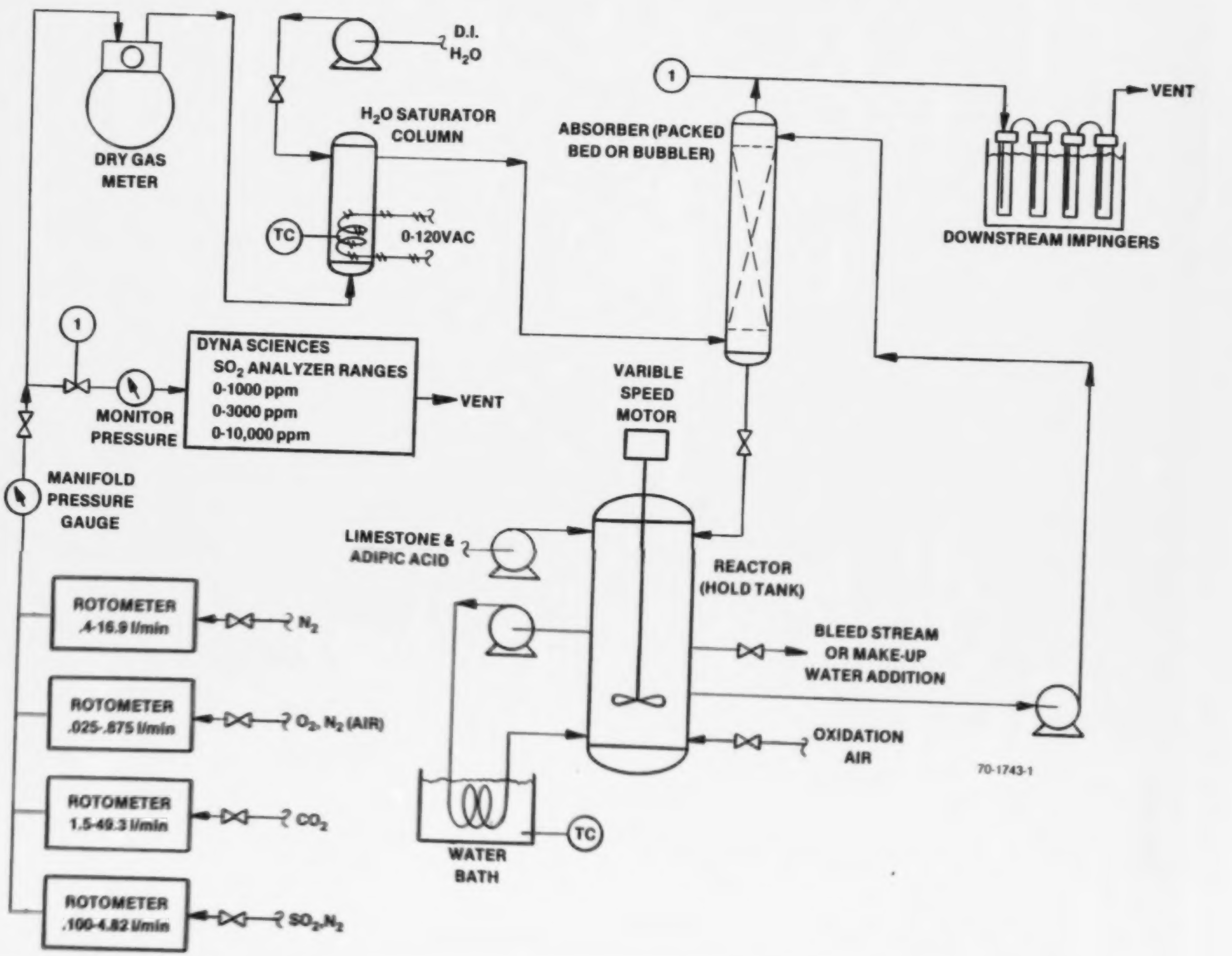
DRY GAS METER
D.I. H_2O
H_2O SATURATOR COLUMN
TC
0-120VAC
1
ABSORBER (PACKED BED OR BUBBLER)
VENT
DOWNSTREAM IMPINGERS
1
DYNA SCIENCES
SO_2 ANALYZER RANGES
0-1000 ppm
0-3000 ppm
0-10,000 ppm
VENT
MONITOR PRESSURE
MANIFOLD PRESSURE GAUGE
VARIBLE SPEED MOTOR
LIMESTONE & ADIPIC ACID
REACTOR (HOLD TANK)
BLEED STREAM OR MAKE-UP WATER ADDITION
OXIDATION AIR
70-1743-1
WATER BATH
TC
ROTOMETER .4-16.9 l/min
N_2
ROTOMETER .025-.875 l/min
O_2, N_2 (AIR)
ROTOMETER 1.5-49.3 l/min
CO_2
ROTOMETER .100-4.82 l/min
SO_2,N_2

Figure 3-1. Schematic diagram of the bench-scale FGD system.

At the start of each run, various materials were added to the hold tank. These materials included deionized water, adipic acid, calcium sulfite seed crystals, NaCl, $MnSO_4 \cdot H_2O$, $Fe_2(SO_4)_3$, fly ash, etc. depending on the purpose of the test. The resulting thin slurry was circulated through the scrubber where it was contacted with flue gas. This procedure was continued for several hours, allowing time for the mass of solids in the hold tank to increase and the concentration of ionic species (particularly $SO_3^=$) to reach a constant level. At this point, a quantitative amount of slurry was withdrawn from the hold tank. Analysis for adipic acid in both the solid and liquid phase, plus data for the hold tank volume, slurry density, and weight percent solids, provided sufficient information to calculate the total mass inventory of adipic acid remaining in the hold tank. At the end of the run, a second sample was withdrawn from the hold tank and the adipic acid inventory was again calculated.

In addition to the initial and final inventories, several other components of the adipic acid mass balance are required in order to compute the degradation rate. These include:

- The mass of adipic acid contained in solids removed from the hold tank during the run (not the solids from the initial or final inventory),
- Makeup adipic acid added to the system to maintain a constant adipic acid concentration, and
- Adipic acid lost from the contactor through entrainment in the flue gas.

Solids were removed during each of the runs to prevent solids accumulation. In Phase 1 and Phase 2 testing, solids were removed by batch filtration. In Phase 3 testing, solids were removed by an in-line filter. Adipic acid entrained in the flue gas was trapped in an impinger immediately downstream of the contactor. Analysis of the liquid from the impinger generally showed only low levels of adipic acid lost due to entrainment of scrubber liquor.

The absolute adipic acid degradation rate can be computed from the mass balance components as follows:

$$Ad_i - Ad_f + Ad_m - Ad_s - Ad_g = Ad_{degraded} \qquad \text{(Eq. 3-1)}$$

where,

Ad_i = Initial adipic acid inventory
Ad_f = Final adipic acid inventory
Ad_m = Makeup adipic acid
Ad_s = Adipic acid removed in filtered solids
Ad_g = Adipic acid entrained in flue gas
$Ad_{degraded}$ = Loss of adipic acid from chemical degradation

Several features were incorporated into the design of the bench-scale unit which facilitated the study of the effects of operating conditions on adipic acid degradation. Some of the more important features are described below:

- Synthetic flue gas, rather than combustion gases, was used during the laboratory phase of testing. This allowed an independent determination of the effect on degradation of components of flue gas such as fly ash.
- Calcium carbonate, rather than limestone was used as the source of alkalinity for baseline testing. This permitted independent study of limestone components (notably trace metals) on adipic acid degradation.
- The system was constructed such that there was no metal in contact with the scrubber slurry. Again, this permitted independent study of the effects of trace metals on the adipic acid degradation rate.

In addition to the measurements required for determining the adipic acid degradation rate, a variety of other variables were monitored:

- pH (controlled),
- Inlet SO_2 concentration (controlled) and outlet SO_2 concentration,

- Percent oxidation in the solids,
- Oxidation air flow rate,
- Temperature of hold tank and gas inlet (controlled),
- Limestone consumption rate,
- Limestone utilization,
- Liquid to gas ratio (L/G),
- Sulfite concentration,
- Chloride concentration (used as a tracer), and
- Trace metals concentration (if added to system).

With this information, the adipic acid degradation rate and other aspects of operation with adipic acid can be related to specific process variables. And, results obtained with the bench-scale system can then be used to anticipate the adipic acid degradation rates in full-scale systems.

3.2 PRESENTATION OF THE BENCH-SCALE ADIPIC ACID DEGRADATION TESTING DATA BASE

The data base for adipic acid degradation bench-scale testing is presented in this section. The data are provided in a series of tables for reference during the discussion of the effects of operating variables on adipic acid degradation which follows this section. Each of the run numbers in the tables which follow contain either the letter R, S, or P. R designates runs done at Radian, S designates runs down on-site at Shawnee, and P designates runs done on-site at Springfield.

The test matrix for the bench-scale scrubber experiments is given in Table 3-1. This table lists the major test conditions and the test objectives for all 43 of the bench-scale runs.

A more detailed listing of operating conditions is provided in Table 3-2. The average operating conditions used to correlate the adipic acid degradation data are listed here.

The results of the chemical analyses performed on individual bench-scale samples are listed in Tables 3-3 and 3-4. The latter table presents the results of gas chromatographic (GC) testing for adipic acid degradation products. Although this data is presented in greater detail in Section 5, some of these results have been utilized in the calculation of the adipic acid degradation rates. Hence, these results are given here.

A summary of the adipic acid degradation rates obtained for each of the bench-scale runs is given in Table 3-5. A listing of the key operating variables is also provided to facilitate inspection of these results. The adipic acid degradation rates are given in three different formats:

1) The absolute adipic acid degradation rate in g/hr,
2) A normalized adipic acid degradation rate in mg/g SO_2 removed, and
3) As an adipic acid degradation rate constant K_d in

$$\frac{\text{mg adipic acid degraded}}{(\text{mole } SO_2 \text{ oxidized})(\text{ppm adipic acid})} \equiv M^{-1}$$

The absolute adipic acid degradation rate in g/hr is the degradation rate determined by mass balance from the bench-scale data. However, it is difficult to use the absolute degradation rate as a means of comparing run data because of the large number of variables which may influence the degradation rate. Also, it is meaningless to use the absolute degradation rate when comparing data from FGD units of different size. To eliminate these deficiencies, the two normalized degradation expressions listed above were developed. Both are based on a simple adipic acid degradation rate model in which the degradation rate is proportional to the liquid phase adipic acid concentration and the sulfite oxidation rate:

(Eq. 3-2)

$$\begin{matrix}\text{Adipic Acid Degradation} \\ \text{Rate, mass/unit time}\end{matrix} = K_d \begin{pmatrix}\text{Adipic Acid} \\ \text{Concentration}\end{pmatrix} \begin{pmatrix}\text{Sulfite Oxidation} \\ \text{Rate, mass/unit time}\end{pmatrix}$$

Here, both the adipic acid degradation rate and the sulfite oxidation rate are dependent on the size of the FGD unit. However, the sulfite oxidation rate is proportional to the product of the SO_2 removal rate and percent

TABLE 3-1. TEST MATRIX FOR BENCH-SCALE SCRUBBER SYSTEM EXPERIMENTS

Test No.	Slurry pH	Oxidation	Other Process Variables Changed	Test Objective
R-1	5.5	Natural	None	Establish high pH baseline at Radian.
R-2	4.6	Natural	None	Establish low pH baseline
R-3	4.6	Natural	None	Replicate low pH baseline
R-4	4.6	Forced	None	Test effect of forced oxidation
R-5	4.6	Forced	High adipic acid conc.	Test effect of adipic acid concentration, compare to R-4.
R-6	4.6	Forced	High adipic acid conc, low inlet SO_2 conc.	Test effect of SO_2 absorption/oxidation rate, compare to R-5.
R-7	5.5	Forced	High adipic acid conc.	Test effect of pH during forced oxidation, compare to R-5.
R-8	5.5	Forced	High adipic acid conc., high sulfite conc.	Test effect of sulfite concentration, compare to R-7.
S-1	4.6	Natural	None	Establish low pH baseline at Shawnee
S-2	4.6	Natural	None	Replicate of low pH baseline.
S-3	4.6	Natural	Nitrogen blanket on reaction tank	Reduce natural oxidation level by reducing entrained O_2 in stirred reaction tank
P-1	4.6	Natural	None	Establish low pH baseline at Springfield
P-2	5.5	Natural	None	Establish high pH baseline at Springfield
P-3	4.6	Natural	$MnSO_4 \cdot H_2O$ added	Test effect of Mn^{+2}, compare to P-1 and P-2.
P-4	4.6	Natural	None	Replicate low pH baseline
R-9	4.6	Natural	None	Re-establish pH baseline tests at both natural and forced oxidation with the bubbler contactor.
R-10	5.1	Natural	None	
R-11	5.5	Natural	None	
R-12	5.1	Forced	None	
R-13	4.6	Forced	None	
R-14	5.1	Forced	$MnSO_4 \cdot H_2O$ added	Evaluate effect of manganese at pH 5.1

(Continued)

TABLE 3-1. (Continued)

Test No.	Slurry pH	Oxidation	Other Process Variables Changed	Test Objective
R-15	4.6	Partial Forced	None	Evaluate effect of intermediate oxidation level
R-16	5.1	Natural	$MnSO_4 \cdot H_2O$ added	Test effect of manganese under natural oxidation conditions
R-17	4.6	Forced	Low Temperature	Evaluate effect of temperature
R-18	5.1	Forced	$MnSO_4 \cdot H_2O$ added	Test effect of manganese at pH 5.1 - replicate run R-14
R-19	5.1	Forced	None	Replicate run R-12
R-20	5.5	Natural	None	Replicate run R-11
R-21	5.5	Natural	High sulfite	Evaluate effect of high sulfite concentration
R-22	5.1	Natural	None	Replicate run R-10 - Baseline for runs R-23, R-24
R-23	5.1	Natural	Low adipic acid conc.	Evaluate effect of low adipic acid concentration
R-24	5.1	Natural	High adipic acid conc.	Evaluate effect of high adipic acid concentration
R-25	4.6	Forced	High temperature	Evaluate effect of temperature
R-26	4.6	Partial Forced	None	Evaluate effect of intermediate oxidation level
R-27	4.6	Forced	$MnSO_4 \cdot H_2O$ added	Test effect of manganese at pH 4.6
R-28	5.1	Forced	Thiosulfate	Test effect of thiosulfate
R-29	5.1	Forced	Limestone	Evaluate effect of limestone
R-30	5.1	Forced	Limestone and fly ash	Evaluate effect of limestone and fly ash
R-31	5.1	Forced	Mn^{+2} and Fe^{+3} added	Evaluate effect of both manganese and iron
R-32	5.1	Natural	High adipic acid conc.	Replicate run R-24
R-33	4.1	Forced	$MnSO_4 \cdot H_2O$ added	Evaluate effect of manganese at pH 4.1
R-34	5.5	Forced	$MnSO_4 \cdot H_2O$ added	Evaluate effect of manganese at pH 5.5
R-35	4.6	Forced	Mn^{+2} + Fe^{+3} added	Evaluate effect of both manganese and iron
R-36	5.1	Forced	High adipic acid conc.	Evaluate effect of high adipic acid concentration

TABLE 3-2. AVERAGE OPERATING CONDITIONS FOR BENCH-SCALE TESTS

Run #	R-1	R-2	R-3	R-4	R-5	R-6	R-7	R-8
Date	5/21/80	5/22/80	5/29/80	7/1/80	7/7/80	7/8/80	7/9/80	7/11/80
Hold tank pH	5.50	4.60	4.60	4.60	4.60	4.60	5.50	5.50
Gas flow rate, scfm	0.568	0.571	0.558	0.554	0.564	0.556	0.568	0.568
Liquid flow rate, ml/min	310	376	367	340	338	340	325	320
L/G, gal/10^3 scf	144	174	174	161	158	158	151	149
Inlet SO_2, ppm	2900	2930	2870	2850	2860	903	2940	2950
Outlet SO_2, ppm	95	430	490	918	370	87	227	302
% SO_2 removal	96.6	85.0	82.6	67.3	86.7	90.1	92.1	89.5
SO_2 removed, g/hr	7.30	6.40	5.96	4.79	6.27	2.07	6.91	6.78
% solids - initial	2.8	1.3	1.7	2.6	2.8	2.8	3.5	2.8
% solids - final	6.3	6.1	6.4	6.2	5.9	4.3	4.6	6.0
Slurry residence time, min	3.3	2.6	2.8	3.5	3.5	2.7	3.9	3.6
Oxidation, mole % (ave)	29	63	35	100	100	100	100	81
Run length, hrs	6	4	9	6	5	7	5	5
Hold tank temp., °F	124	125	122	125	125	125	125	125
Adipic in filtrate (ave), ppm	2370	3394	2625	2900	9340	10080	8960	9800
Adipic in solids (ave), ppm	2008	0	307	0	296	334	478	1635
$SO_3^=$ - (ave), ppm	390	3327	2570	414	1198	1007	904	2450
Mn^{+2} - (ave), ppm	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Fe^{+3} - (ave), ppm	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

(Continued)

TABLE 3-2. (Continued)

Run #	S-1	S-2	S-3	P-1	P-2	P-3	P-4
Date	8/6/80	8/7/80	8/8/80	8/21/80	8/23/80	9/5/80	9/6/80
Hold tank pH	4.60	4.60	4.60	4.60	5.50	4.60	4.60
Gas flow rate, scfm	0.568	0.574	0.576	0.539	0.524	0.535	0.525
Liquid flow rate, ml/min	374	376	376	308	316	326	316
L/G, gal/10^3 scf	174	173	172	151	159	161	159
Inlet SO_2, ppm	2380	2500	2470	2370	2370	2240	2230
Outlet SO_2, ppm	515	510	520	720	215	475	530
% SO_2 removal	78.4	79.6	78.9	69.6	90.9	78.8	76.2
SO_2 removed, g/hr	4.77	5.15	5.06	4.01	5.09	4.26	4.02
% solids - initial	1.2	3.9	0.9	0.9	2.0	0.8	0.7
% solids - final	7.3	10.1	6.1	5.0	6.6	7.2	5.9
Slurry residence time, min	2.5	2.6	2.6	3.6	3.5	3.1	3.3
Oxidation, mole % (ave)	28	17	28	12	7	22	11
Run length, hrs	8	8	6	8	8	8	6
Hold tank temp., °F	125	125	125	125	125	125	125
Adipic in filtrate (ave), ppm	3011	3118	2736	2847	2435	3120	3280
Adipic in solids (ave), ppm	1625	0	1410	2730	7126	3130	5609
$SO_3^=$ - (ave), ppm	2450	1885	2430	3129	515	2585	3115
Mn^{+2} - (ave), ppm	<0.1	<0.1	<0.1	1.3	0.7	12.7	1.6
Fe^{+3} - (ave), ppm	NA	NA	NA	NA	NA	NA	NA

(Continued)

TABLE 3-2. (Continued)

Run #	R-9	R-10	R-11	R-12	R-13	R-14	R-15
Date	2/2/81	2/4/81	2/9/81	2/10/81	2/11/81	2/12/81	2/24/81
Hold tank pH	4.6	5.1	5.5	5.1	4.6	5.1	4.6
Gas flow rate, scfm	0.669	0.664	0.664	0.669	0.668	0.673	0.664
Liquid flow rate, ml/min	266	266	245	245	245	245	245
L/G, gal/10^3 scf	105	106	98	97	97	96	98
Inlet SO_2, ppm	2687	2690	2636	2700	2684	2673	2600
Outlet SO_2, ppm	930	620	243	330	640	353	800
% SO_2 removal	64.5	76.3	90.5	87.5	75.5	86.4	69.2
SO_2 removed, g/hr	5.63	6.63	7.68	7.66	6.56	7.55	5.73
% solids - initial	2.53	3.09	2.46	2.55	2.58	2.99	2.2
% solids - final	3.50	5.25	3.18	3.31	3.43	3.10	3.3
Slurry residence time, min	7.5	7.5	8.2	8.2	8.2	8.2	8.2
Oxidation, mole % (ave)	11.7	9.7	11.0	77.4	100	100	42.5
Run length, hrs	22	22	12	18.5	18	20	21.5
Hold tank temp., °F	126	126	125	126	126	125	125
Adipic in filtrate (ave), ppm	2438	2263	2416	2016	2096	2791	2714
Adipic in solids (ave), ppm	3154	5077	6093	763	42	200	1180
$SO_3^=$ - (ave), ppm	2778	1160	532	1227	1203	low	2825
Mn^{+2} - (ave), ppm	0.0	0.0	0.0	0.0	0.0	21.1	0.0
Fe^{+3} - (ave), ppm	0.0	0.0	0.0	0.0	0.0	0.0	0.0

(Continued)

TABLE 3-2. (Continued)

Run #	R-16	R-17	R-18	R-19	R-20	R-21	R-22
Date	2/26/81	3/4/81	3/5/81	3/9/81	3/10/81	3/12/81	3/16/81
Hold tank pH	5.1	4.6	5.1	5.1	5.5	5.5	5.1
Gas flow rate, scfm	0.662	0.671	0.636	0.668	0.667	0.663	0.665
Liquid flow rate, ml/min	245	245	245	245	245	245	245
L/G, gal/10^3 scf	98	97	102	97	97	98	98
Inlet SO_2, ppm	2720	2655	2715	2615	2750	2755	2605
Outlet SO_2, ppm	667	278	390	440	375	450	335
% SO_2 removal	75	90	86	83	86	84	87
SO_2 removed, g/hr	6.55	7.71	7.15	7.02	7.67	7.38	7.30
% solids - initial	3.1	3.4	3.1	4.1	2.9	3.2	2.7
% solids - final	3.0	1.9	3.4	3.7	3.8	5.1	3.0
Slurry residence time, min	8.2	8.7	8.1	8.3	8.2	8.3	8.20
Oxidation, mole % (ave)	11.0	100	100	100	11.5	23.0	20
Run length, hrs	22	19	22	20	22	22	20
Hold tank temp., °F	124	93	125	124	124	125	125
Adipic in filtrate (ave), ppm	2105	2449	2059	1659	2640	3023	2893
Adipic in solids (ave), ppm	4815	0	75	78	6517	321	5092
$SO_3^=$ - (ave), ppm	1265	1410	low	1461	485	2605	1355
Mn^{+2} - (ave), ppm	2.4	0.0	5.8	0.0	0.0	0.0	0.0
Fe^{+3} - (ave), ppm	0.0	0.0	0.0	0.0	0.0	0.0	0.0

(Continued)

TABLE 3-2. (Continued)

Run #	R-23	R-24	R-25	R-26	R-27	R-28	R-29
Date	3/17/81	3/24/81	3/31/81	4/2/81	4/8/81	4/9/81	4/14/81
Hold tank pH	5.1	5.1	4.6	4.6	4.6	5.1	5.1
Gas flow rate, acfm	0.669	0.669	0.681	0.674	0.685	0.683	0.689
Liquid flow rate, ml/min	245	245	245	245	245	245	245
L/G, gal/10^3 acf	97	97	95	96	95	95	94
Inlet SO_2, ppm	2615	2610	2671	2688	2759	2720	2866
Outlet SO_2, ppm	850	550	1032	967	1123	967	500
% SO_2 removal	67	79	61	64	59	64.4	82.6
SO_2 removed, g/hr	5.66	6.64	5.34	5.55	5.46	5.73	7.87
% solids - initial	2.2	2.8	2.7	2.4	2.6	2.1	3.4
% solids - final	1.9	2.0	2.2	1.7	2.0	1.4	1.8
Slurry residence time, min	8.2	8.3	8.0	8.3	8.1	8.0	8.4
Oxidation, mole % (ave)	13.0	27.5	100	100	100	3.4	100
Run length, hrs	22	18	22	22	20	19	20
Hold tank temp., °F	125	123	146	126	125	125	125
Adipic in filtrate (ave), ppm	876	6777	2246	1660	2800	2567	2959
Adipic in solids (ave), ppm	1703	11422	59	64	144	6542	1252
$SO_3^=$ - (ave), ppm	1155	1447	900	791	low	1168	low
Mn^{+2} - (ave), ppm	0.0	0.0	0.0	0.0	15.3	0.0	4.7
Fe^{+3} - (ave), ppm	0.0	0.0	0.0	0.0	0.0	0.0	<0.6

(Continued)

TABLE 3-2. (Continued)

Run #	R-30	R-31	R-32	R-33	R-34	R-35	R-36
Date	4/15/81	4/21/81	4/23/81	4/27/81	5/5/81	5/4/81	5/7/81
Hold tank pH	5.1	5.1	5.1	4.1	5.5	4.6	5.1
Gas flow rate, scfm	0.684	0.647	0.574	0.679	0.694	0.602	0.692
Liquid flow rate, ml/min	245	245	245	245	245	245	245
L/G, gal/10^3 scf	94	100	113	95	93	107	93
Inlet SO_2, ppm	2889	2702	2685	2756	2660	2735	2705
Outlet SO_2, ppm	477	673	500	1165	655	847	354
% SO_2 removal	83.5	75.1	81.4	57.7	75.4	69.0	86.9
SO_2 removed, g/hr	7.97	6.25	6.46	5.14	6.70	6.30	7.86
% solids - initial	5.1	4.2	2.9	2.6	3.7	2.3	2.6
% solids - final	2.2	2.0	1.4	2.0	1.6	1.6	1.6
Slurry residence time, min	8.3	8.2	8.6	8.0	8.1	8.1	8.5
Oxidation, mole % (ave)	100	100	12.0	99	100	98	100
Run length, hrs	20	24	19	23	18	24	20
Hold tank temp., °F	125	125	125	125	125	124	124
Adipic in filtrate (ave), ppm	3313	2031	7158	2675	1822	2419	5622
Adipic in solids (ave), ppm	1183	156	16385	0	809	360	178
$SO_3^{=}$ - (ave), ppm	Low	Low	1236	Low	Low	Low	1678
Mn^{+2} - (ave), ppm	4.6	5.6	0.0	17.9	8.8	16.2	0.0
Fe^{+3} - (ave), ppm	<0.7	<0.8	0.0	0.0	0.0	0.0	<1.4

TABLE 3-3. INDIVIDUAL ANALYSES OF BENCH-SCALE SAMPLES

Run #	Time	Adipic in Liquid, ppm	Adipic in Solids, ppm	Percent Oxidation	Sulfite, ppm	Other Analyses, ppm
R-1	Initial	3337	1265	35.8	513	$[Cl^-]$ = 4926
	Mid-point	2612	2866	13.6	312	$[Cl^-]$ = 4394
	Mid-point	1978	2053	--	--	$[Cl^-]$ = 3362
	Final	1535	1847	30.3	344	$[Cl^-]$ = 3014
	Average	2370	2008	29.2	390	$[Cl^-]$ = 3924
R-2	Initial	3835	0	60.3	3900	$[Cl^-]$ = 5923
	Final	2953	0	65.0	2753	$[Cl^-]$ = 5727
	Average	3394	0	62.7	3327	$[Cl^-]$ = 5825
R-3	Initial	3346	951	16.4	3549	$[Cl^-]$ = 5108
	Mid-point	2836	422	32.9	2691	$[Cl^-]$ = 4272
	Mid-point	2390	135	39.9	2123	$[Cl^-]$ = 3621
	Final	1955	0	50.0	2232	$[Cl^-]$ = 3251
	Average	2625	307	35.0	2570	$[Cl^-]$ = 4063
R-4	Initial	2736/(3794)	0	--	172	$[Cl^-]$ = 2220
	Mid-point	2450/(3229)	0	99.0	389	$[Cl^-]$ = 1940
	Final	2129	0	99.6	704	$[Cl^-]$ = 1710
	Average	2900	0	99.3	414	$[Cl^-]$ = 1965
R-5	Initial	9973	--	96.1	1814	$[Cl^-]$ = 986
	Mid-point	7656/(11695)	--	--	984	$[Cl^-]$ = 842
	Final	8016	--	99.3	1009	$[Cl^-]$ = 710
	Average	9340	296	97.7	1108	$[Cl^-]$ = 845
R-6	Initial	10395	--	99.2	778	$[Cl^-]$ = 661
	Mid-point	9178/(11717)	--	99.3	1025	$[Cl^-]$ = 661
	Final	9224	--	99.3	1198	$[Cl^-]$ = 591
	Average	10080	334	99.3	1007	$[Cl^-]$ = 645
R-7	Initial	8313	--	98.5	580	$[Cl^-]$ = 3660
	Mid-point	5823/(13042)	--	98.8	876	$[Cl^-]$ = 2980
	Final	8666	--	98.7	1282	$[Cl^-]$ = 2290
	Average	8960	478	98.7	904	$[Cl^-]$ = 2978
R-8	Initial	10207	334	--	2415	$[Cl^-]$ = 1443
	Mid-point	7824/(12060)	2105	80.5	2111	$[Cl^-]$ = 1201
	Final	9120	1996	82.2	1637	$[Cl^-]$ = 1056
	Average	9800	1635	81.4	2069	$[Cl^-]$ = 1225

(Continued)

TABLE 3-3. (Continued)

Run #	Time	Adipic in Liquid, ppm	Adipic in Solids, ppm	Percent Oxidation	Sulfite, ppm	Other Analyses, ppm
S-1	Initial	3455	5408	--	3150	$[Cl^-] = 5655$
	Mid-point	2985	449	36.0	2290	$[Cl^-] = 4915$
	Final	2619	194	19.4	2070	$[Cl^-] = 4664$ $[Mn^{+2}] = 0.03$
	Average	3011	1625	27.7	2450	$[Cl^-] = 5037$
S-2	Initial	3215	0	--	2040	$[Cl^-] = 2433$
	Mid-point	3133	0	16.3	1930	$[Cl^-] = 2400$
	Final	2989	0	17.7	1640	$[Cl^-] = 2634$ $[Mn^{+2}] = 0.06$
	Average	3118	0	17.0		$[Cl^-] = 2467$
S-3	Initial	2961	2847	--	2840	$[Cl^-] = 4701$
	Mid-point	2665	1168	31.2	2380	$[Cl^-] = 4299$
	Final	2653	456	24.2	2120	$[Cl^-] = 4823$ $[Mn^{+2}] = 0.08$
	Average	2736	1410	27.7	2430	$[Cl^-] = 4531$
P-1	Initial	3456	2090	--	3816	$[Cl^-] = 4497$ $[Mn^{+2}] = 1.01$
	Mid-point	2718	2910	--	2915	$[Cl^-] = 3918$ $[Mn^{+2}] = 1.20$
	Final	2497	3010	11.5	2870	$[Cl^-] = 3706$ $[Mn^{+2}] = 1.86$
	Average	2847	2730	11.5	3129	$[Cl^-] = 4010$ $[Mn^{+2}] = 1.32$
P-2	Initial	3280	6670		593	$[Cl^-] = 4719$ $[Mn^{+2}] = 0.95$
	Mid-point	2268	7850		473	$[Cl^-] = 3963$ $[Mn^{+2}] = 0.63$
	Final	1925	6132	7.4	519	$[Cl^-] = 3807$ $[Mn^{+2}] = 0.42$
	Average	2435	7126	7.4	515	$[Cl^-] = 4113$ $[Mn^{+2}] = 0.66$
P-3	Initial	3590	4720		3520	$[Cl^-] = 4580$ $[Mn^{+2}] = 18.3$
	Mid-point	2990	3025		2360	$[Cl^-] = 4160$ $[Mn^{+2}] = 13.8$
	Final	2910	1750	21.8	2360	$[Cl^-] = 4150$ $[Mn^{+2}] = 4.9$
	Average	3120	3130	21.8	2585	$[Cl^-] = 4263$ $[Mn^{+2}] = 12.7$
P-4	Initial	3410	6207		3590	$[Cl^-] = 4690$ $[Mn^{+2}] = 0.94$
	Final	3150	5010	11.4	2640	$[Cl^-] = 4620$ $[Mn^{+2}] = 2.22$
	Average	3280	5609	11.4	3115	$[Cl^-] = 4655$ $[Mn^{+2}] = 1.58$

(Continued)

TABLE 3-3. (Continued)

Run #	Time	Adipic in Liquid, ppm	Adipic in Solids, ppm	Percent Oxidation	Sulfite, ppm	Other Analyses, ppm
R-9	Initial	2552	3730	11.7	2850	$[Cl^-] = 413$
	Final	2324	2577	11.7	2706	$[Cl^-] = 341$
	Average	2438	3154	11.7	2778	$[Cl^-] = 377$
R-10	Initial	2387	5582	11.3	1130	$[Cl^-] = 486$
	Final	2139	4572	8.1	1190	$[Cl^-] = 376$ $[Ca^{+2}] = 1040$
	Average	2263	5077	9.7	1160	$[Cl^-] = 431$
R-11	Initial	2542	4228	13.8	544	$[Cl^-] = 469$
	Final	2290	7957	8.2	520	$[Cl^-] = 430$
	Average	2416	6093	11.0	532	$[Cl^-] = 449$
R-12	Initial	2099	201	99.4	864	$[Cl^-] = 422$
	Final	1932	1324	55.4	1590	$[Cl^-] = 380$
	Average	2016	763	77.4	1227	$[Cl^-] = 401$
R-13	Initial	2321	100	100.0	857	$[Cl^-] = 419$
	Final	1870	0	100.0	1540	$[Cl^-] = 376$
	Average	2096	42	100.0	1204	$[Cl^-] = 398$
R-14	Initial	2592	146	100.0	Low	$[Cl^-] = 408$ $[Mn^{+2}] = 10.5$
	Final	2989	253	100.0	Low	$[Mn^{+2}] = 31.7$
	Average	2791	200	100.0	Low	$[Cl^-] \simeq 390$ $[Mn^{+2}] = 21.1$
R-15	Initial	2477	1023	47.0	2830	$[Cl^-] = 412$
	Final	2951	1338	38.0	2820	$[Cl^-] = 359$
	Average	2714	1181	42.5	2825	$[Cl^-] = 385$
R-16	Initial	2347	5600	12.0	1190	$[Cl^-] = 383$ $[Mn^{+2}] = 2.6$
	Final	1862	4030	10.0	1340	$[Cl^-] = 330$ $[Mn^{+2}] = 2.2$
	Average	2105	4815	11.0	1265	$[Cl^-] = 357$ $[Mn^{+2}] = 2.4$
R-17	Initial	2496	0	100.0	1420	$[Cl^-] = 398$
	Final	2401	10	100.0	1400	$[Cl^-] = 320$
	Average	2449	0	100.0	1410	$[Cl^-] = 359$

(Continued)

TABLE 3-3. (Continued)

Run #	Time	Adipic in Liquid, ppm	Adipic in Solids, ppm	Percent Oxidation	Sulfite, ppm	Other Analyses, ppm
R-18	Initial	2396	83	100.0	Low	$[Mn^{+2}] = 5.4$
	Final	1722	66	100.0	Low	$[Mn^{+2}] = 6.2$
	Average	2059	75	100.0	Low	$[Cl^-] \simeq 390$ $[Mn^{+2}] = 5.8$
R-19	Initial	1936	52	100.0	632	
	Final	1382	103	100.0	2290	
	Average	1659	78	100.0	1461	$[Cl^-] \simeq 390$
R-20	Initial	2565	3142	13.0	440	
	Final	2715	7892	10.1	530	
	Average	2640	5517	11.5	485	$[Cl^-] \simeq 390$
R-21	Initial	2689	0	32.0	3160	
	Final	3357	913	14.0	2050	
	Average	3023	321	23.0	2605	$[Cl^-] \simeq 390$
R-22	Initial	2604	3178	12.0	1320	
	Final	3181	3006	28.0	1390	
	Average	2893	3092	20.0	1355	$[Cl^-] = 354$ $[Ca^{+2}] = 1920$
R-23	Initial	875	1542	13.0	1043	
	Final	877	1864	13.0	1267	
	Average	876	1703	13.0	1155	$[Cl^-] = 324$ $[Ca^{+2}] = 1300$
R-24	Initial	6279	14870	12.0	1324	
	Final	7274	7972	43.0	1570	
	Average	6777	11420	27.5	1447	$[Cl^-] = 354$ $[Ca^{+2}] = 3080$
R-25	Initial	2498	0	100.0	335	
	Final	1993	133	100.0	1466	
	Average	2246	67	100.0	901	$[Cl^-] \simeq 390$
R-26	Initial	2229	81	100.0	341	
	Final	1091	46	100.0	1240	
	Average	1660	64	100.0	791	$[Cl^-] \simeq 390$

(Continued)

TABLE 3-3. (Continued)

Run #	Time	Adipic in Liquid, ppm	Adipic in Solids, ppm	Percent Oxidation	Sulfite, ppm	Other Analyses, ppm
R-27	Initial	2638	147	100.0	Low	$[Mn^{+2}] = 14.6$
	Final	2961	141	100.0	Low	$[Mn^{+2}] = 16.2$
	Average	2800	144	100.0	Low	$[Cl^-] \simeq 390$ $[Mn^{+2}] = 15.3$
R-28	Initial	2514	4855	6.3	945	[thiosulfate] = 279
	Final	2619	8229	0.4	1390	[thiosulfate] = 222
	Average	2567	6542	3.4	1168	$[Cl^-] \simeq 390$ [thiosulfate] = 251
R-29	Initial	2446	801	100.0	Low	$[Mn^{+2}] = 5.8$ $[Fe^{+3}] = 0.8$
	Final	3471	1702	100.0	Low	$[Mn^{+2}] = 3.5$ $[Fe^{+3}] < 0.4$
	Average	2959	1252	100.0	Low	$[Cl^-] \simeq 390$ $[Mn^{+2}] = 4.7$ $[Fe^{+3}] \leq 0.6$
R-30	Initial	2636	552	100.0	Low	$[Mn^{+2}] = 4.6$ $[Fe^{+3}] < 0.9$
	Final	3989	1813	100.0	Low	$[Mn^{+2}] = 4.5$ $[Fe^{+3}] \leq 0.4$
	Average	3313	1183	100.0	Low	$[Cl^-] \simeq 390$ $[Mn^{+2}] = 4.6$ $[Fe^{+3}] \leq 0.6$
R-31	Initial	2380	103	100.0	Low	$[Mn^{+2}] = 5.2$ $[Fe^{+3}] < 0.5$
	Final	1682	208	100.0	Low	$[Mn^{+2}] = 6.0$ $[Fe^{+3}] \leq 1.0$
	Average	2031	156	100.0	Low	$[Cl^-] \simeq 390$ $[Mn^{+2}] = 5.6$ $[Fe^{+3}] \leq 0.7$
R-32	Initial	7649	18030	11.5	1210	
	Final	6667	14740	12.4	1262	
	Average	7158	16385	12.0	1236	$[Cl^-] \simeq 390$
R-33	Initial	2526	0	100.0	Low	$[Mn^{+2}] = 15.8$
	Final	2824	54	98.0	Low	$[Mn^{+2}] = 19.9$
	Average	2575	27	99.0	Low	$[Cl^-] \simeq 390$ $[Mn^{+2}] = 17.9$
R-34	Initial	2312	809	100.0	Low	$[Mn^{+2}] = 10.7$
	Final	1331	—	100.0	Low	$[Mn^{+2}] = 6.8$
	Average	1822	809	100.0	Low	$[Cl^-] \simeq 390$ $[Mn^{+2}] = 8.8$
R-35	Initial	2402	393	97.0	Low	$[Mn^{+2}] = 15.1$ $[Fe^{+3}] < 2.0$
	Final	2436	327	98.0	Low	$[Mn^{+2}] = 17.2$ $[Fe^{+3}] \leq 1.1$
	Average	2419	360	98.0	Low	$[Cl^-] \simeq 390$ $[Mn^{+2}] = 16.2$ $[Fe^{+3}] \leq 1.5$
R-36	Initial	6561	178	100.0	644	
	Final	4683	—	99.0	2712	
	Average	5622	178	100.0	1678	$[Cl^-] \simeq 390$

TABLE 3-4. RESULTS OF GC ANALYSES FOR FINAL BENCH-SCALE FILTRATE SAMPLE ADIPIC ACID DEGRADATION PRODUCTS

Run #	Acid Concentrations[1], ppm									Bench-Scale Scrubber Operating Conditions
	Acetic[2]	Propionic[2]	Butyric[2]	Valeric[2]	Oxalic[3]	Malonic[3]	Succinic[3]	Glutaric[3]	Adipic[3]	
R-9	<4	<3	<2	7	<63	<33	51	<28	2880	pH 4.6, natural oxidation, 22 hours
R-10	<3	<2	<2	23	<24	<13	27	<11	3430	pH 5.1, natural oxidation, 22 hours
R-11	<4	<3	<2	54	<32	<17	32	<14	2630	pH 5.5, natural oxidation, 12 hours
R-12	<3	15	<2	138	<29	80	31	23	2760	pH 5.1, forced oxidation, 18.5 hours
R-13	<4	17	<2	95	<30	66	37	73	2310	pH 4.6, forced oxidation, 18 hours
R-14	<3	<3	<2	52	<29	29	54	400	5310	pH 5.1, forced oxidation, 21 ppm Mn, 20 hours
R-15	<4	72	243	154	<16	<8	<10	<7	3280	pH 4.6, partial forced oxidation, 21.5 hours
R-16	<3	4	4	65	<15	<8	<9	<6	1700	pH 5.1, natural oxidation, 2 ppm Mn, 22 hours
R-17	<4	55	17	188	<16	22	<10	<7	3280	pH 4.6, forced oxidation, low temperature, 19 hours
R-18	<4	4	7	56	16	<9	255	622	2650	pH 5.1, forced oxidation, 5 ppm Mn, 22 hours
R-19	<4	238	<2	440	<16	238	62	74	1840	pH 5.1, forced oxidation, 20 hours
R-20	<4	<3	<2	330	<16	<9	<10	<7	5250	pH 5.5, natural oxidation, 22 hours
R-21	<4	<3	<2	124	<16	<8	<10	<7	2870	pH 5.5, natural oxidation, high sulfite, 22 hours
R-22	<4	<3	<2	290	<15	<8	<10	<7	3970	pH 5.1, natural oxidation, 20 hours
R-23	<3	<3	7	<2	<15	<8	<9	<6	1700	pH 5.1, natural oxidation, low adipic conc., 22 hours
R-24	<4	<3	<2	211	<14	<7	<9	<6	11580	pH 5.1, natural oxidation, high adipic conc., 18 hours
R-25	102	<3	<2	215	<15	109	63	234	2480	pH 4.6, forced oxidation, high temperature, 22 hours
R-26	69	157	195	262	<15	48	<10	55	1310	pH 4.6, forced oxidation, 22 hours
R-27	92	<3	<2	<2	<16	<8	<10	86	3000	pH 4.6, forced oxidation, 15 ppm Mn^{+2}, 20 hours
R-28	<4	<3	<3	<2	<18	<9	<10	<8	2940	pH 5.1, forced oxidation, thiosulfate, 19 hours
R-30	<4	29	13	27	<15	68	160	561	3080	pH 5.1, forced oxidation, Springfield limestone plus fly ash, 20 hours
R-31	<4	<3	10	20	<16	76	136	468	1550	pH 5.1, forced oxidation, 6 ppm Mn^{+2}, 2 ppm Fe^{+3}, 24 hours
R-33	<3	<2	<2	4	<14	<7	12	108	1960	pH 4.1, forced oxidation, 18 ppm Mn^{+2}, 23 hours

[1] Acid concentrations have been calculated for the undiluted filtrate.

[2] Monobasic acids: Average relative standard deviation = ±4% for 3 or more determinations.

[3] Dibasic acids: Uncertainty due to dilution and variable extraction efficiencies = 10-20%.

TABLE 3-5. SUMMARY OF BENCH-SCALE SYSTEM ADIPIC ACID DEGRADATION RESULTS

Run No.	Degradation of Adipic Acid as: Absolute Degradation, g/hr	Degradation of Adipic Acid as: mg Adipic Degraded / g SO_2 removed	Degradation Rate Constant K_d, M^{-1}	Uncertainty[1] Level, ±%	Run Characteristics
R-1	0.068	9.4	0.86	54	Natural oxidation, pH 5.5 (baseline)
R-2	0.030	4.7	0.14	116	Natural oxidation, pH 4.6 (baseline)
R-3	0.018	3.1	0.21	70	Natural oxidation, pH 4.6 (baseline)
R-4	0.30	63	1.38	7.5	Forced oxidation, pH 4.6 (baseline)
R-5	0.66	105	0.74	14	Forced oxidation, pH 4.6, High adipic acid conc. (baseline)
R-6	0.30	143	0.92	19	Forced oxidation, pH 4.6, high adipic acid conc., low SO_2 inlet conc. (baseline)
R-7	0.66	96	0.69	16	Forced oxidation, pH 5.5, high adipic acid conc. (baseline)
R-8	0.50	75	0.59	20	Forced oxidation, pH 5.5, high adipic acid conc., high sulfite conc.
S-1	0.041	8.6	0.66	37	Natural oxidation, pH 4.6
S-2	0.061	11.9	1.43	26	Natural oxidation, pH 4.6
S-3	0.053	10.5	0.89	36	Natural oxidation, pH 4.6, exclude O_2 from hold tank
P-1	0.026	6.5	1.27	67	Natural oxidation, pH 4.6
P-2	0.032	6.3	2.23	50	Natural oxidation, pH 5.5
P-3	0.018	4.2	0.40	97	Natural oxidation, pH 4.6, manganese
P-4	0.027	6.6	1.15	91	Natural oxidation, pH 4.6
R-9	0.025	4.5	1.01	39	Natural oxidation, pH 4.6 (baseline)
R-10	0.028	4.2	1.22	35	Natural oxidation, pH 5.1 (baseline)
R-11	0.016	2.0	0.49	121	Natural oxidation, pH 5.5 (baseline)
R-12	0.189	24.7	1.01	5.5	Partial forced oxidation, pH 5.1 (baseline)
R-13	0.298	45.4	1.39	3.3	Forced oxidation, pH 4.6 (baseline)
R-14	0.136	18.1	0.41	9.0	Forced oxidation, pH 5.1, manganese

[1] Uncertainty level reflects experimental uncertainty in the absolute degradation rate only.

(Continued)

TABLE 3-5. (Continued)

Run No.	Degradation of Adipic Acid as: Absolute Degradation, g/hr	Degradation of Adipic Acid as: $\frac{\text{mg Adipic Degraded}}{\text{g SO}_2\text{ Removed}}$	Degradation Rate Constant K_d, M^{-1}	Uncertainty[1] Level, ±%	Run Characteristics
R-15	0.131	22.8	1.27	8.3	Partial forced oxidation, pH 4.6 (baseline)
R-16	0.038	5.9	1.62	23	Natural oxidation, pH 5.1, low manganese
R-17	0.154	20.0	0.52	7.7	Forced oxidation, pH 4.6, low temperature
R-18	0.145	20.2	0.63	5.5	Forced oxidation, pH 5.1, manganese
R-19	0.346	49.3	1.90	2.1	Forced oxidation, pH 5.1 (baseline)
R-20	0.041	5.3	1.12	30	Natural oxidation, pH 5.5 (baseline)
R-21	0.079	10.7	0.98	16	Natural oxidation, pH 5.5, high sulfite
R-22	0.076	10.4	1.16	17	Natural oxidation, pH 5.1 (baseline)
R-23	0.015	2.7	1.53	24	Natural oxidation, pH 5.1, low adipic acid conc. (baseline)
R-24	0.074	11.2	0.38	48	Natural oxidation, pH 5.1, high adipic acid conc. (baseline)
R-25	0.436	81.7	2.33	1.9	Forced oxidation, pH 4.6, high temperature
R-26	0.295	53.2	2.05	2.3	Forced oxidation, pH 4.6 (baseline)
R-27	0.047	8.6	0.20	25	Forced oxidation, pH 4.6, manganese
R-28	0.010	1.7	1.26	123	Forced oxidation, pH 5.1, thiosulfate
R-29	0.236	30.0	0.65	5.7	Forced oxidation, pH 5.1, limestone (manganese)
R-30	0.204	25.6	0.49	7.5	Forced oxidation, pH 5.1, limestone + fly ash (manganese)
R-31	0.097	15.5	0.49	7.6	Forced oxidation, pH 5.1, manganese + iron
R-32	0.123	19.0	1.42	30	Natural oxidation, pH 5.1, high adipic acid conc. (baseline)
R-33	0.047	9.1	0.22	21	Forced oxidation, pH 4.1, manganese
R-34	0.178	26.6	0.93	5.1	Forced oxidation, pH 5.5, manganese
R-35	0.076	12.1	0.33	12	Forced oxidation, pH 4.6, manganese + iron
R-36	0.640	81.4	0.93	4	Forced oxidation, pH 5.1, high adipic acid conc. (baseline)

[1] Uncertainty level reflects experimental uncertainty in the absolute degradation rate only.

solids oxidation. Note that the percent oxidation of the solids represents both the chemical composition of the solids and the percentage of absorbed SO_2 which is oxidized to sulfate. With this substitution, the above model can be rearranged to give:

(Eq. 3-3)

$$\frac{\text{Mass of Adipic Acid Degraded}}{\text{Mass of } SO_2 \text{ Removed}} = K_d \begin{pmatrix}\text{Adipic Acid}\\ \text{Concentration}\end{pmatrix} \begin{pmatrix}\text{Percent Solids}\\ \text{Oxidation}\end{pmatrix}$$

This is the normalized adipic acid degradation rate given in Table 3-5. It is useful in comparing degradation data from different sources because it is given as a function of variables which are independent of unit size.

The value of the adipic acid degradation rate constant, K_d, has also been given in Table 3-5. According to the above rate expression, K_d should have a constant value regardless of the adipic acid concentration or the level of oxidation. This feature makes K_d extremely useful in evaluating the effects of operating variables which have not been included in the proposed rate model. Of course, the assumed proportionality of the degradation rate to the adipic acid concentration and the level of sulfite oxidation must be verified by experiment.

K_d is calculated from the bench-scale data using the following equation:

(Eq. 3-4)

$$\left[K_d, \frac{(\text{mg adipic acid degraded})}{(\text{mole } SO_2 \text{ oxidized})(\text{ppm adipic acid})}\right] = \frac{\begin{pmatrix}\text{adipic acid}\\ \text{degradation rate}\end{pmatrix}, \frac{\text{mg adipic degraded}}{\text{g } SO_2 \text{ removed}} \Big) \left(64 \frac{\text{g } SO_2}{\text{mole } SO_2}\right)}{\begin{pmatrix}\text{mole fraction}\\ \text{solids oxidation}\end{pmatrix}\begin{pmatrix}\text{adipic acid}\\ \text{concentration, ppm}\end{pmatrix}}$$

By convention, the units of the degradation rate constant can be simplified as follows:

$$\frac{(\text{mg adipic acid degraded})}{(\text{mole } SO_2 \text{ oxidized})(\text{ppm adipic acid})} = \frac{(\text{mg } \cancel{\text{adipic acid}} \text{ degraded})}{(\text{mole } SO_2 \text{ oxidized})\left(\frac{\text{mg } \cancel{\text{adipic acid}}}{\text{liter}}\right)}$$

$$= \frac{1}{\left(\frac{\text{moles } SO_2 \text{ oxidized}}{\text{liter}}\right)}$$

$$= M^{-1}$$

Note that for the units of K_d, moles rather than grams of SO_2 have been used. The purpose of this change is to make the value of K_d numerically equivalent to that reported by Rochelle in his investigation of adipic acid degradation.

3.3 THE EFFECT OF OPERATING VARIABLES ON ADIPIC ACID DEGRADATION

The effects of individual operating variables are discussed in this section. The variables considered here include the following:

- SO_2 absorption/oxidation rate,
- Adipic acid concentration,
- pH,
- Trace metals (manganese, iron),
- Limestone and limestone + fly ash (versus reagent grade $CaCO_3$),
- Boiler flue gas (versus synthetic flue gas),
- Temperature,
- Thiosulfate (as an additive), and
- Sulfite concentration.

Analysis of the data base for determining the effects of these variables is facilitated by dividing the data base into several subsets; each designed to illustrate the effects of a different variable(s). The first, and largest, data subset are the baseline runs. The variables examined in these runs include only the sulfite absorption/oxidation rate, the adipic acid concentration, and pH. The specific runs in the baseline data set include:

R-1
R-2
R-3
R-4
R-5
R-6
R-7
R-9
R-10
R-11
R-12
R-13
R-15
R-19
R-20
R-22
R-23
R-24
R-26
R-32
R-36

The results of these runs are discussed in Section 3.3.1.

The second data subset examines the effects of trace metals and trace metals versus pH and includes runs done with manganese, manganese plus iron, limestone, and limestone plus fly ash. The specific runs in the trace metals data set include:

R-14
R-16
R-18
R-27
R-29
R-30
R-31
R-33
R-34
R-35

Note that pH was also a variable included in this data set. The results of these runs are discussed in Section 3.3.2.

The next data subset includes the bench-scale runs done on-site at Shawnee and Springfield. These runs include:

S-1
S-2
S-3
P-1
P-2
P-3
P-4

The Shawnee runs are characterized by the use of Shawnee flue gas and $CaCO_3$ as the alkaline species. The Springfield runs are characterized by the use of Springfield flue gas and limestone. The results of the runs in this data set are described in Section 3.3.3.

Runs R-13, R-17, and R-25 were designed to evaluate the effect of temperature on the adipic acid degradation rate. These results are presented in Section 3.3.4.

The effects of some other additivies were also investigated. In run R-28, thiosulfate, a sulfite oxidation inhibitor, was added to the hold tank. In runs R-8 and R-21, Na_2SO_4 was added. The purpose of adding the Na_2SO_4 was to increase the equilibrium sulfite concentration. The results of these tests are given in Section 3.3.5.

3.3.1 Results of Baseline Adipic Acid Degradation Testing

As previously described, the baseline data subset includes only those runs in which the effects of the SO_2 absorption/oxidation rate, the adipic acid concentration, and pH were studied. The purpose of these tests was to evaluate the individual effects of these primary variables. In addition, the baseline data set provides a reference point when looking at the effects of other variables.

The most striking feature of the baseline results is the effect of the sulfite oxidation rate on the adipic acid degradation rate. As an example, consider the results of runs R-9 and R-13 (see Table 3-5). Both runs were done at pH 4.6 and had roughly equivalent adipic acid concentrations. Run R-9, however, was a natural oxidation run (11.7% average oxidation) while run R-13 was a forced oxidation run (100% oxidation). The resulting degradation rates of 4.5 mg/g SO_2 absorbed for R-9 and 45.4 mg/g SO_2 absorbed for run R-13 illustrate the importance of sulfite oxidation to degradation. This effect is seen throughout the baseline data set.

In the above example, the degradation rates were compared to the percent oxidation in the solids. The percent oxidation is a measure of the percentage of absorbed SO_2 which is oxidized to sulfate. Strictly speaking, the absolute degradation rate is a function of the total SO_2 oxidation rate where the total SO_2 oxidation rate is proportional to the product of the SO_2 removal rate and the percent solids oxidation. It is convenient, however, to normalize the absolute degradation by the SO_2 removal rate so the expressions used for the degradation rate are independent of the size of the FGD unit. For example, consider the results of runs R-5 and R-6. These runs were quite similar except that the inlet SO_2 concentration used in run R-6 was considerably lower than that of run R-5. Selected results for these runs are given below:

Run #	Total SO_2 Oxidized, g/hr	Absolute Adipic Degradation, g/hr	Degradation mg/g SO_2 Removed	Degradation Rate Constant K_d, M^{-1}
R-5	6.27	0.66	105	0.74
R-6	2.07	0.30	143	0.92

These results illustrate that while the SO_2 oxidation rates and the absolute degradation rates are quite different, the normalized degradation rates are much closer to each other (particularly for K_d which normalizes differences in the adipic acid concentrations).

Data illustrating the effect of the adipic acid concentration on the adipic acid degradation rate are given in Table 3-6. The same data are shown graphically in Figure 3-2. The data in Table 3-6 illustrate that an increase in the adipic acid concentration generally result in an increase in the degradation rate. The increase in degradation, however, does not seem to be directly proportional to the increase in the adipic acid concentration. Figure 3-2 is a plot of K_d versus the adipic acid concentration for the data in Table 3-6. Note that the lines representing the best fit of the data (by least squares linear regression) shown in Figure 3-2 both have negative slopes.

In the development of K_d, linearity between the degradation rate and the adipic acid concentration is assumed. If this is the case, then K_d would be independent of the adipic acid concentration and the regressions in a plot such as that in Figure 3-2 would be horizontal lines with zero slope. This does not appear to be the case.

A computerized statistical analysis was performed on the baseline data set. There were several reasons for performing this analysis:

- The results of such an analysis would indicate which variables were statistically significant with regard to degradation,

TABLE 3-6. EFFECT OF ADIPIC ACID CONCENTRATION ON THE ADIPIC ACID RATE CONSTANT K_d

Run #	Adipic Acid Concentration, ppm	Degradation Rate Constant K_d, M^{-1}	pH	Comments
R-23	876	1.529	5.1	Natural oxidation
R-10	2263	1.223	5.1	Natural oxidation
R-22	2893	1.155	5.1	Natural oxidation
R-24	6777	0.384	5.1	Natural oxidation
R-32	7158	1.419	5.1	Natural oxidation
R-26	1706	2.049	4.6	Forced oxidation
R-19	1722	1.903	5.1	Forced oxidation
R-13	2159	1.388	4.6	Forced oxidation
R-4	2900	1.382	4.6	Forced oxidation
R-36	5622	0.927	5.1	Forced oxidation
R-7	8960	0.690	5.5	Forced oxidation
R-5	9340	0.736	4.6	Forced oxidation
R-6	10080	0.920	4.6	Forced oxidation - Low SO_2 inlet

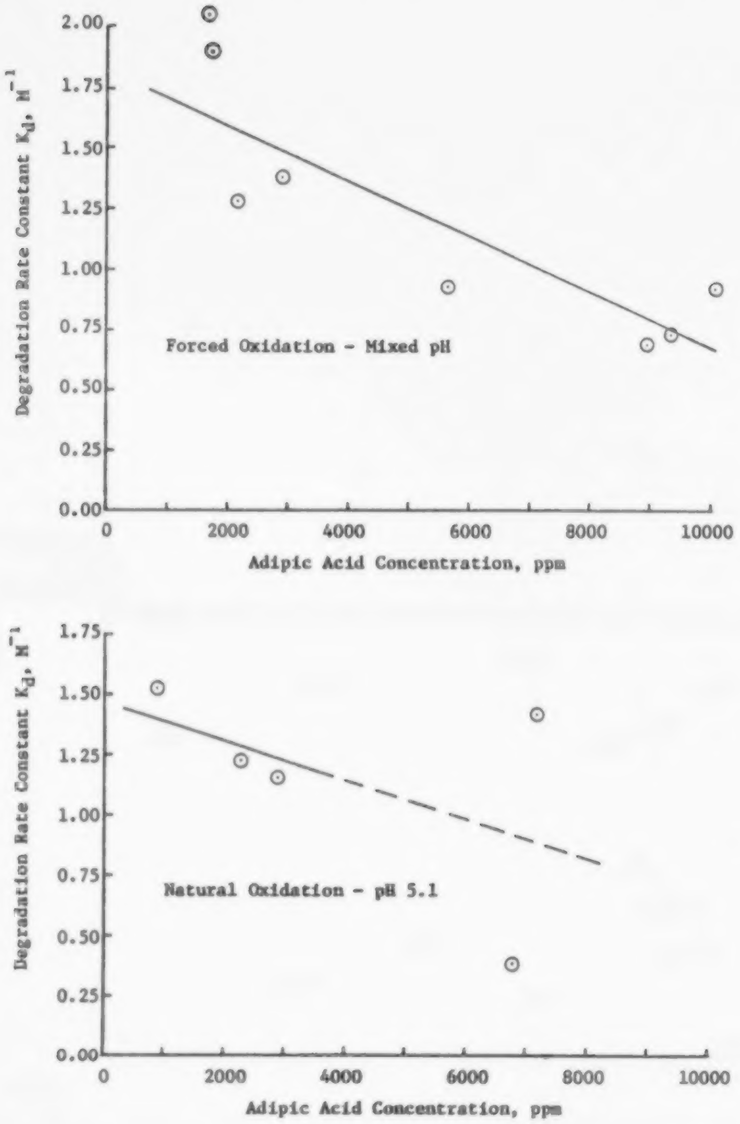

Figure 3-2. Variation in the adipic acid degradation rate constant (K_d) with adipic acid concentration.

- After determining the most significant variables, the computer would determine the coefficients of a rate model which could be used to predict degradation rates, and
- The degradation model could then be used to compare the effects of variables evaluated in subsequent testing.

Variables tested for statistical significance included the sulfite absorption/oxidation rate, the adipic acid concentration, pH, and the sulfite concentration. The form of the model used to analyze the baseline adipic acid degradation results is given below:

(Eq. 3-5)

$$\left(\begin{array}{c}\text{adipic acid}\\ \text{degradation rate}\end{array}, \frac{\text{mg adipic acid degraded}}{\text{g SO}_2\text{ removed}}\right) = A_1 \left(\begin{array}{c}\text{percent solids}\\ \text{oxidation}\end{array}\right)^{A_2} \left(\begin{array}{c}\text{adipic acid}\\ \text{concentration, ppm}\end{array}\right)^{A_3} \left(\begin{array}{c}\text{sulfite ion}\\ \text{concentration, ppm}\end{array}\right)^{A_4} \left(\begin{array}{c}\text{hydrogen ion}\\ \text{concentration(pH), M}\end{array}\right)^{A_5}$$

The results of this analysis showed that only the sulfite absorption/oxidation rate and the adipic acid concentration were statistically significant. pH was not found to affect the degradation rate. Since the equilibrium sulfite concentration is closely related to pH, it is not surprising that the sulfite concentration was also found to be statistically insignificant with regard to degradation.

The computer determined the coefficients of significant variables using a weighted linear regression. The weighted regression was used in order to incorporate the experimental uncertainty in the analysis. That is, more significance was placed on those data points which had the least experimental uncertainty. Only the uncertainty in the degradation rate, however, was considered in the analysis. The correlation resulting from this analysis is as follows:

(Eq. 3-6)

$$\begin{array}{l}\text{adipic acid}\\ \text{degradation rate,}\end{array}\ \text{mg/g SO}_2\text{ removed} = 0.00308 \left(\begin{array}{c}\text{adipic acid}\\ \text{concentration, ppm}\end{array}\right)^{0.5542} \left(\text{percent oxidation}\right)^{1.185}$$

(correlation coefficient, r^2, = 0.960)

The adipic acid degradation rate given in equation 3-6 can be substituted into the expression for K_d given in equation 3-5. The resulting equation for K_d in terms of percent oxidation and the adipic acid concentration is given below:

(Eq. 3-7)

$$K_d,\ M^{-1} = 19.7\ \frac{(\text{percent oxidation})^{0.185}}{(\text{adipic acid concentration, ppm})^{0.446}}$$

The correlation given in equation 3-6 is shown graphically in Figure 3-3. The range of operating variables included in the correlation are:

Degradation rate: 2.0 - 143 mg/g SO_2 removed
Percent oxidation: 9.7 - 100%
Adipic acid concentration: 876-10080 ppm

The correlation given in equation 3-6 illustrates several of the effects discussed earlier in this section. First, the degradation rate appears to be roughly directly proportional to the level of sulfite oxidation. Also, the adipic acid degradation rate appears to be roughly proportional to the square root of the adipic acid concentration. The latter results tend to conflict with the most commonly proposed degradation mechanism which suggests a directly proportional relationship between degradation and the adipic acid concentration(6). The data, however, clearly indicate that from an operational standpoint, direct proportionality is not observed.

3.3.2 Effect of Manganese on Adipic Acid Degradation

This section contains the results of runs done with manganese, manganese plus iron, limestone, and limestone plus fly ash. The common factor involved in all of these runs was the presence of manganese ions in the scrubber liquor. Only the results of runs performed in the laboratory at Radian are included in this section. Some of the runs performed with the bench-scale scrubber at Springfield also contained manganese and these results are reported in Section 3.3.3.

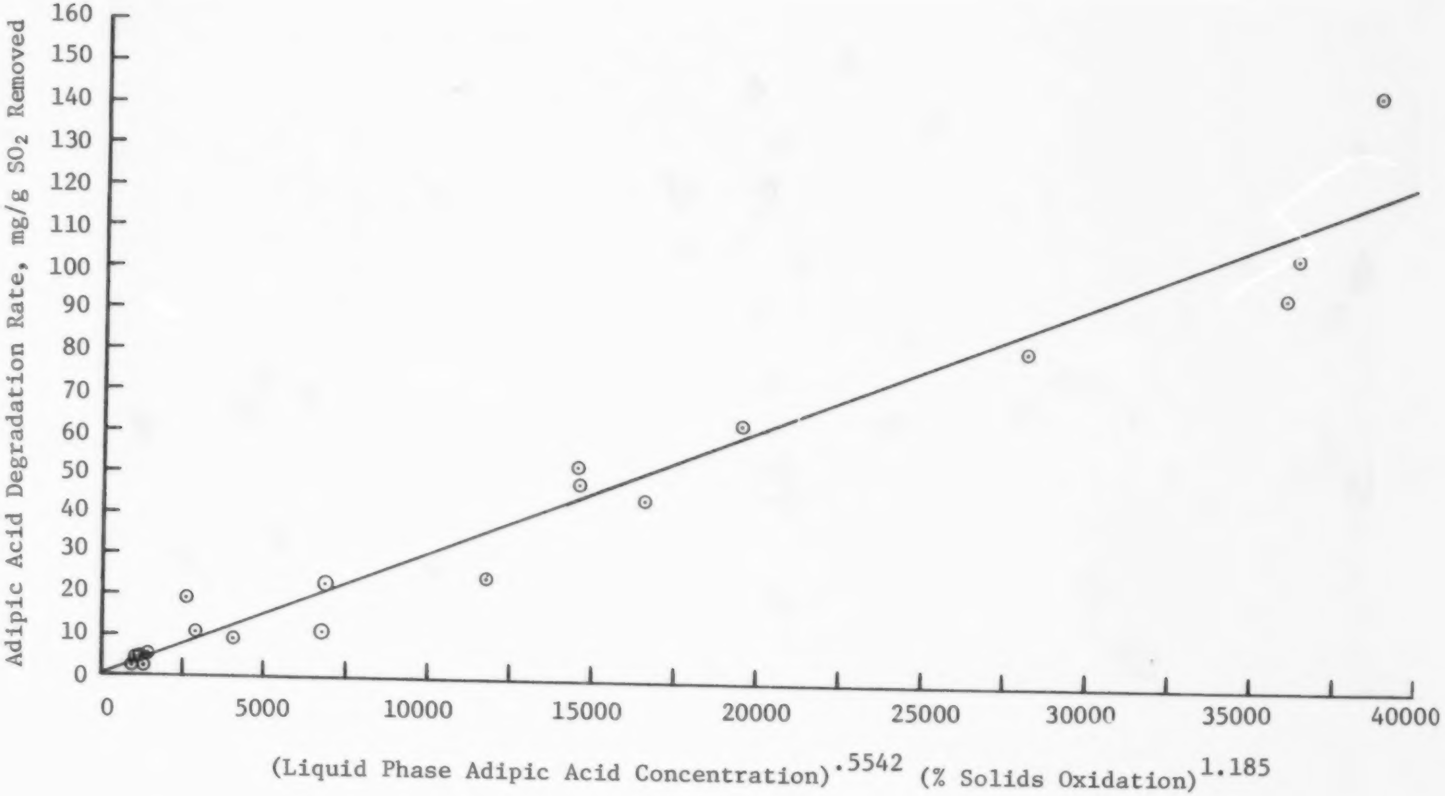

Figure 3-3. Correlated relationship between the adipic acid degradation rate, the liquid phase adipic acid concentration, and the percent solids oxidation for the baseline data set.

Selected results from manganese data subset are listed in Table 3-7. The most striking result from these tests is the reduction in the adipic acid degradation rate due to the presence of manganese ions. The reduction in the adipic acid degradation rate for all forced oxidation runs ranges from 42.5 to 85.4 percent below the values predicted from the adipic acid degradation rate correlation developed in Section 3.3.1. A natural oxidation run (R-16) was also attempted. However, almost none of the manganese could be held in solution and the observed degradation rate was actually above the predicted value.

The data in Table 3-7 also indicate a significant effect of pH on the degradation rate. This result is illustrated graphically in Figure 3-4 which shows the value of the rate constant K_d for the forced oxidation runs versus pH. Note that the curve indicated in Figure 3-4 is intended only to illustrate the trend of the data and is not based on a formal mathematical relationship. The pH dependence seen in Figure 3-4 was not observed in the baseline data set in which manganese was not present.

Some limited information on the effect of the manganese concentration can be obtained by examining the data at pH 5.1. Here, a reduction in the degradation rate of 59.1 percent below the predicted level was obtained with only 6 ppm manganese. At a concentration of 21 ppm, a 69.3 percent reduction was observed. Greater reductions in the degradation rate could probably be obtained at still higher concentrations of manganese.

The differing levels of manganese listed for each of the bench-scale tests can be attributed, in part, to the solubility of manganese. That is, not all of the manganese added to the hold tank (as $MnSO_4 \cdot H_2O$) was recovered as soluble manganese. Generally speaking, manganese was found to be more soluble at lower pH. Also, more manganese was held in solution in the forced oxidation runs than in the natural oxidation run at the same pH. Data illustrating these effects is given in Table 3-8.

TABLE 3-7. RESULTS OF BENCH-SCALE RUNS WITH MANGANESE, IRON, LIMESTONE, AND FLY ASH

Run #	Degradation Rate Constant K_d, M^{-1}	Degradation as mg/g SO_2 Removed	Predicted Degradation Rate, mg/g SO_2 Removed[1]	% Reduction from Predicted Degradation	pH	Run Conditions
Runs with manganese only ($CaCO_3$)						
R-33	0.22	9.14	56.6	83.9	4.1	$[Mn^{+2}]$ = 18 ppm forced oxidation
R-27	0.20	8.61	58.7	85.4	4.6	$[Mn^{+2}]$ = 15 ppm forced oxidation
R-14	0.41	18.0	58.6	69.3	5.1	$[Mn^{+2}]$ = 21 ppm forced oxidation
R-18	0.63	20.3	49.5	59.1	5.1	$[Mn^{+2}]$ = 6 ppm forced oxidation
R-34	0.93	26.6	46.3	42.5	5.5	$[Mn^{+2}]$ = 9 ppm forced oxidation
R-16	1.62	5.9	3.7	-60	5.1	$[Mn^{+2}]$ = 2 ppm natural oxidation
Runs with manganese and iron ($CaCO_3$)						
R-35	0.33	12.1	52.9	77.1	4.6	$[Mn^{+2}]$ = 16 ppm; $[Fe^{+3}]$ <1.5 forced oxidation
R-31	0.49	15.5	49.2	68.5	5.1	$[Mn^{+2}]$ = 6 ppm; $[Fe^{+3}]$ = 2 ppm forced oxidation
Runs with Springfield limestone						
R-29	0.65	30.0	60.6	50.5	5.1	$[Mn^{+2}]$ = 5 ppm; $[Fe^{+3}]$ <0.6 ppm forced oxidation
R-30	0.49	25.6	64.5	60.3	5.1	$[Mn^{+2}]$ = 5 ppm; $[Fe^{+3}]$ <0.6 ppm forced oxidation + fly ash

[1] Predicted degradation rate from baseline correlation:

$$\text{adipic acid degradation rate, mg/g } SO_2 \text{ removed} = 0.00308 \left(\begin{matrix}\text{adipic acid}\\ \text{concentration, ppm}\end{matrix}\right)^{0.5542} \left(\text{percent oxidation}\right)^{1.185} \qquad \text{(Eq. 3-6)}$$

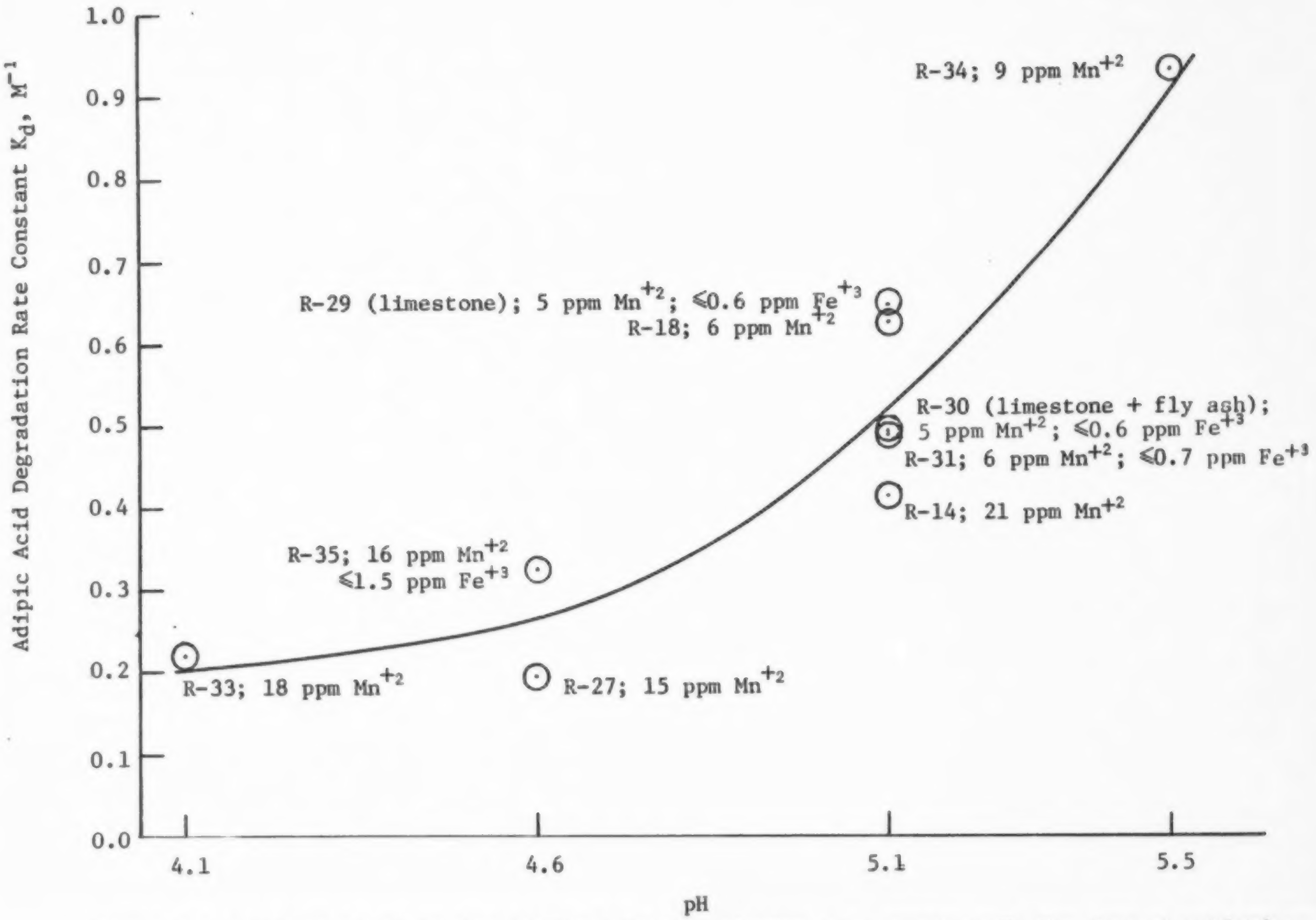

Figure 3-4. Effect of pH on the adipic acid degradation rate constant K_d for forced oxidation runs with manganese, manganese + iron, limestone, and limestone + fly ash. (Adipic acid concentrations for these runs varied from 1820 to 3310 ppm.)

TABLE 3-8. EFFECT OF pH AND OXIDATION LEVEL ON MANGANESE SOLUBILITY

Run #	Expected Mn^{+2} Conc., ppm[1]		Actual Mn^{+2} Conc., ppm		% of Total Mn^{+2} Recovered in Liquid[2]	pH	% Solids Oxidation	
	Initial	Final	Initial	Final				
R-33	15.9	16.8	15.8	19.9	118	4.1	99	
R-27	15.8	19.6	14.4	16.2	82.7	4.6	100	
R-14[3]	19.0	32.7	10.5	31.7	96.9	5.1	100	
R-18	5.2	9.8	5.4	6.2	63.9	5.1	100	
R-34	23.2	32.1	10.7	6.8	21.2	5.5	100	
R-16	16.0	28.5	2.6	2.2	7.7	5.1	11	Natural oxidation
R-35	16.7	19.7	15.1	17.2	87.3	4.6	98	Runs with Mn^{+2} and Fe^{+3}
R-31	10.4	14.8	5.2	6.0	40.7	5.1	100	

[1] Based on amount of manganese (as $MnSO_4 \cdot H_2O$) added to the hold tank.

[2] Based on total manganese mass balance.

[3] Manganese reagent used in this run analyzed at only 70% of the expected manganese content. Mass balance results from this run are uncertain.

At the end of run R-33 (pH 4.1 - forced oxidation $+ Mn^{+2}$), the pH was slowly increased from 4.1 to 5.5. A dark brown manganese precipitate formed on the surface of the hold tank at about pH 5.2. This material could be redissolved by decreasing the pH. Also, the first evidence of precipitation was at the outlet of the heater coil where the slurry temperature was about 5°F above the hold tank temperature. This result indicates an inverse relationship between the solubility of this manganese precipitate and temperature.

An inspection of available literature indicates that Mn^{+2} is probably not oxidized to the +4 or +7 oxidation state under scrubber conditions (2)(3). Oxidation to the +4 state with free oxygen is possible at pH values above 8.5 (3). However, if Mn^{+} was oxidized to the +4 oxidation state, it would immediately precipitate as MnO_2 which could not redissolve under scrubber conditions. Therefore, the manganese precipitate probably is composed of Mn^{+2}. Since less manganese could be held in solution during natural oxidation tests, the precipitate is most likely $MnSO_3$. This possibility was not verified by chemical analysis.

The above considerations regarding the solubility and the effect upon the adipic acid degradation rate of manganese are significant because limestone often contains significant quantities of manganese. An example of this is given in Table 3-9 which is a trace metals analysis of Springfield limestone. This is the limestone used for bench-scale runs R-29 and R-30 (and runs P-1 through P-4 reported in Section 3.3.3) and for the full-scale adipic acid demonstration at City Utilities Southwest Power Station in Springfield, MO. The data in Table 3-9 show this limestone contains 430 ppm manganese. Thus, the equilibrium concentration of dissolved manganese is probably determined, in part, by solubility considerations.

The results of runs R-29 and R-30 show an equilibrium concentration of about 5 ppm Mn^{+2} at pH 5.1-forced oxidation using limestone. Bench-scale results from runs done at Springfield show similar results with an equilibrium

TABLE 3-9. ICAPES[1] SCREENING ANALYSIS OF SPRINGFIELD LIMESTONE

Element	Concentration, ppm	Element	Concentration, ppm
Al	57	Mo	<1.0
Ba	420	Na	200
Co	<3.0	Ni	<1.5
Cu	<0.5	P	<90
Cr	<0.5	Si	41
Fe	160	Sr	<0.1
K	110	Ti	<0.5
Li	<0.1	V	<1.5
Mg	1400	Y	20
Mn	430	Zn	15

[1] Inductively coupled argon plasma emissions spectroscopy

concentrations of 4.3 ppm Mn^{+2} at pH 5.2-forced oxidation. In natural oxidation runs, however, maximum manganese concentrations were less than 2 ppm at pH 4.6 and pH 5.5.

From the standpoint of the adipic acid degradation rate, the results seen for runs R-29 (limestone) and R-30 (limestone + fly ash) are about the same as runs done at the same pH with $CaCO_3$ and added manganese. There appears to be an additional reduction in the degradation rate in run R-30 over that observed in run R-29 due to the presence of fly ash. However, the difference between these two results is within the experimental uncertainty and may not be statistically significant. A separate run, evaluating the effect of fly ash alone, was not performed.

Several runs were attempted with Fe^{+3} ions in the hold tank. The results of these runs were somewhat unexpected. In one experiment, approximately 20 ppm Fe^{+3} was added to the hold tank after run R-32 (pH 5.1, natural oxidation) was completed. The first effect observed was an immediate drop in pH. After approximately two hours, the pH had dropped to 4.1, the sulfite concentration had increased to 7040 ppm, and Fe^{+3} ions were still present in the hold tank. Excess quantities of $CaCO_3$ were added to the hold tank but had no effect on pH indicating that a limestone blinding phenomenon was occurring. At this point, the system was switched to a forced oxidation mode. This procedure was unsuccessful in solving the blinding problem. After about an hour, manganese, an oxidation promoter, was added to the hold tank. This procedure was also unsuccessful in solving the blinding problem. Finally, $Ca(OH)_2$ was added to the hold tank. This procedure was successful in raising the pH back to 5.1. And, $CaCO_3$ addition was successful in maintaining this pH value. Analysis of a sample taken at this time showed that essentially no iron remained in solution. These results are similar to those first observed during bench-scale testing at Springfield in which several natural oxidation runs with iron were attempted. As was the case in the laboratory testing, the only method found to solve the blinding problem was to precipitate out the iron with $Ca(OH)_2$.

Several forced oxidation runs with iron were also attempted. Although the limestone blinding problem was not observed here, little, if any iron could be held in solution. Two forced oxidation runs, R-31 and R-35, were performed with both manganese and iron in the hold tank. The purpose of these runs was to observe a possible synergistic effect between manganese and iron in reducing the adipic acid degradation rate. The results of these runs (Table 3-7) show that essentially no iron could be held in solution and the observed degradation rates were about as expected for the manganese concentration and pH utilized.

Part of the scope of work on this program was the development of analytical techniques for identifying and quantifying adipic acid degradation products. The techniques developed include (1) gas chromatography (GC) for analysis of mono- and dicarboxylic acids in the liquid phase and hydrocarbons in the flue gas, and (2) ion exclusion chromatography (ICE) for analysis of liquid phase mono- and dicarboxylic acids. These techniques were used to analyze for adipic acid degradation products in many of the bench-scale samples. One of the most striking results was the high levels of glutaric and succinic acid found in samples from runs in which manganese ions were present in the hold tank. These results, given in Table 3-10, show that from 13 to 41 mole percent of the total amount of degraded adipic acid was recovered as glutaric acid and that up to 15 mole percent of the degraded adipic acid was recovered as succinic acid. In all of the other bench-scale runs for which degradation product analyses were available, less than four mole percent of the degraded adipic acid was recovered as glutaric acid. This preferential formation of glutaric acid, and to a lesser extent succinic acid, is significant in that glutaric and succinic acid buffer scrubber solutions in a manner similar to adipic acid. The change in the degradation product distribution may also indicate a change in the adipic acid degradation mechanism due to the presence of manganese.

The data developed during this section have been used to predict the adipic acid degradation rates for the full-scale adipic acid demonstration

TABLE 3-10. RESULTS OF GC AND ICE ANALYSES FOR GLUTARIC AND SUCCINIC ACID IN THE FINAL FILTRATE BENCH-SCALE SAMPLES[1] FOR THE MANGANESE DATA SUBSET RUNS

	Analyses for Glutaric Acid, ppm[2]			Analyses for Succinic Acid, ppm[2]			Mole % Adipic Acid Degraded to:		
Run #	GC	ICE	Average	GC	ICE	Average	Glutaric	Succinic	Run Conditions[3]
R-14	400	358 378	380	64	69 86	73	27	6	pH 5.1; 20 hours $[Mn^{+2}]$ = 21 ppm
R-18	662	659 744 461	620	265	194 155	205	37	14	pH 5.1; 22 hours $[Mn^{+2}]$ = 5 ppm
R-25	234	231	233	65	25	45			
R-27	86	47	67	<10	---	<10	13	<2	pH 4.6; 20 hours $[Mn^{+2}]$ = 15 ppm
R-29	---	740	740	---	---	---	29	--	pH 5.1; Limestone; 20 hours $[Mn^{+2}]$ = 3 ppm; $[Fe^{+3}] \leq 0.6$ ppm
R-30	561	725	643	160	---	160	30	8	pH 5.1; Limestone + Fly ash; 20 hours $[Mn^{+2}]$ = 5ppm; $[Fe^{+3}] \leq 0.6$ ppm
R-31	468	512	490	156	---	156	41	15	pH 5.1; 24 hours $[Mn^{+2}]$ = 6 ppm; $[Fe^{+3}] \leq 0.7$ ppm
R-33	108	124	116	32	---	32	21	6	pH 4.1; 23 hours $[Mn^{+2}]$ = 18 ppm
R-34	---	636	636	---	---	--	37	--	pH 5.5; 18 hours $[Mn^{+2}]$ = 9 ppm
R-35	---	185	185	---	---	--	21	--	pH 4.6; 24 hours $[Mn^{+2}]$ = 16 ppm; $[Fe^{+3}] \leq 1.5$ ppm

[1] The analyses shown here are for the final filtrate samples. The degradation products may have accumulated over a total operating period which included an average four hour line out period plus the run time listed under the run conditions.

[2] Analytical uncertainty for both GC and ICE techniques about ±20%.

[3] All forced oxidation runs.

program in Springfield, MO. Three determinations of the adipic acid degradation rate have been made for forced oxidation runs at Springfield conducted from February through March, 1981. The adipic acid degradation rates observed during this period were 7.6 and 11.6 mg/g SO_2 removed (8). The appropriate run conditions for this test period are summarized below:

Adipic acid concentration: 2500 ppm (average)
pH : 5.0 - 5.3
Percent oxidation : 100%
Manganese concentration : ≃40 ppm
Hold tank temperature : 120 - 130°F

The results required for estimating the adipic acid degradation rate are contained in Figure 3-4. From these results, an adipic acid rate constant of $K_d = 0.35$ is about what would be expected, given the pH and manganese concentrations used in the Springfield full-scale tests. The adipic acid degradation rate can be estimated using Equation 3-4.

$$\begin{array}{l}\text{adipic acid degradation} \\ \text{rate, mg/g } SO_2 \text{ removed}\end{array} = \frac{K_d \text{ (adipic acid concentration, ppm)} \begin{pmatrix}\text{mole fraction} \\ \text{oxidation}\end{pmatrix}}{64}$$

$$= \frac{(0.35)(2500)(1.0)}{64}$$

$$= 13.7 \text{ mg/g } SO_2 \text{ removed}$$

This value is reasonably close to the adipic acid degradation rates of 7.6 and 11.6 mg/g SO_2 removed observed in the full-scale tests.

3.3.3 Results of Bench-Scale Testing at Shawnee and Springfield

This section contains the results of bench-scale testing at the Shawnee test facility in Paducah, KY and at the City Utilities Southwest Power Station in Springfield, MO. The purpose of these tests was to:

- Determine if a component in the flue gas was responsible for the low adipic acid degradation rates reported by Shawnee during low pH testing, and to

- Develop data at Springfield which could be used to predict the adipic acid degradation rate during full-scale demonstration testing.

A total of three runs (S-1, S-2, and S-3) were performed at Shawnee. Ten runs (P-1 through P-10) were performed at Springfield. However, adipic acid degradation rates could not be determined for runs P-5 through P-10 due to a problem with sample stability.

The runs conducted at Shawnee were all natural oxidation runs at pH 4.6. $CaCO_3$, rather than limestone, was used as the source of alkalinity. In the runs conducted in Springfield, limestone obtained on-site was used as the source of alkalinity. Natural oxidation runs at Springfield were conducted at pH 4.6 and pH 5.5. In run P-3, $MnSO_4 \cdot H_2O$ was added to the hold tank.

Selected results for this series of runs is given in Table 3-11. These results include the adipic acid degradation rate, the rate constant K_d, and the predicted baseline degradation rate based on the correlation developed in Section 3.3.1. The runs listed as "S" designate runs performed at Shawnee while "P" designates runs performed at Springfield. The results show that the lowest value of K_d and the largest deviation from the predicted degradation rate occurs in run P-3. This is the run in which manganese was added to the hold tank. The value of $K_d = 0.4$ for this run is similar to that obtained for forced oxidation runs with manganese at the same pH which indicates that manganese is effective in reducing adipic acid degradation under both forced and natural oxidation conditions.

The adipic acid degradation rates observed for the remainder of the runs listed in Table 3-11 seem to be about evenly distributed around the predicted degradation rates. This indicates that neither the fly ash present in the Shawnee runs nor the limestone and fly ash used in the Springfield runs had an effect on the adipic acid degradation rate. The large experimental uncertainty associated with these runs results from the relatively low degradation rates observed and the six to eight hour run times employed.

TABLE 3-11 RESULTS OF BENCH-SCALE ADIPIC ACID DEGRADATION TESTING AT SHAWNEE AND SPRINGFIELD

Run #	Adipic Acid Degradation Rate Constant K_d, M^{-1}	Adipic Acid Degradation Rate, mg/g SO_2 Removed	Predicted Adipic Acid Degradation Rate, mg/g SO_2 Removed[1]	% Difference Between Actual and Predicted Degradation Rates	Run Conditions
S-1	0.66	8.60 ±37%	13.4	-56	pH 4.6; natural oxidation $[Mn^{+2}]$ 0.1 ppm
S-1	1.43	11.8 ±26%	7.6	36	pH 4.6; natural oxidation $[Mn^{+2}]$ 0.1 ppm
S-3	0.89	10.5 ±36%	12.7	-21	pH 4.6; natural oxidation (N_2 blanket over hold tank) $[Mn^{+2}]$ 0.1 ppm
P-1	1.27	6.48 ±66%	4.6	29	pH 4.6; natural oxidation $[Mn^{+2}] = 1.3$ ppm
P-2	2.23	6.29 ±49%	2.5	60	pH 5.5; natural oxidation $[Mn^{+2}] = 0.7$ ppm
P-3	0.40	4.23 ±98%	10.3	-144	pH 4.6; natural oxidation ($MnSO_4 \cdot H_2O$ added to hold tank) $[Mn^{+2}] = 12.7$ ppm
P-4	1.12	6.72 ±91%	4.9	27	pH 4.6; natural oxidation $[Mn^{+2}] = 1.6$ ppm

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[1] Predicted degradation rate from baseline correlation:

$$\text{adipic acid degradation rate, mg/g } SO_2 \text{ removed} = 0.00308 \left(\begin{matrix}\text{adipic acid}\\ \text{concentration, ppm}\end{matrix}\right)^{0.5542} (\text{percent oxidation})^{1.185} \qquad \text{(Eq. 3-6)}$$

Limestone was used for the bench-scale tests performed at Springfield. This same limestone was used in forced oxidation tests (runs R-29 and R-30) at Radian. In the laboratory forced oxidation tests, significant reductions in the adipic acid degradation rate were observed with equilibrium manganese concentrations of 5 to 6 ppm (see Section 3.3.2). With the natural oxidation conditions employed at Springfield, the equilibrium concentrations of manganese were less than 1.6 ppm. This was apparently below the concentration of manganese necessary to cause a decrease in degradation rate from the level predicted from the baseline correlation.

Additional forced oxidation tests with limestone at Springfield showed higher equilibrium concentrations of manganese. However, the adipic acid degradation rates for these tests could not be determined due to a problem with sample stability. Samples from runs P-1 through P-4 were analyzed on-site at Springfield shortly after sample collection. Samples from later tests, however, were analyzed at Radian approximately one week after sample collection. Routine multiple analyses of these samples indicated that continuing adipic acid degradation was occuring. Reanalysis of samples from the Shawnee tests and previous laboratory bench-scale tests showed that significant continuing decomposition seemed to be unique to the Springfield samples.

A laboratory test program was initiated to determine the factors involved in the decomposition of the Springfield samples. The results of these tests showed that adipic acid decomposition occured in the presence of both hydrogen peroxide and manganese ions. Hydrogen perioxide (H_2O_2) was added to the bench-scale filtrate samples to remove sulfite ions which interfere with the IC analysis of adipic acid. The decomposition of the Springfield samples was the result of the peroxide and the manganese ions present in the sample. Following this determination, the sampling procedures were changed such that sulfite removal, via peroxide, was performed immediately prior to sample analysis.

A distinct second peak was observed during IC analyses of samples from the decomposition test program. This material did not correspond to any of the identified adipic acid degradation products and was probably composed of the so-called Shawnee mystery compound. A more detailed description of the laboratory decomposition test results is presented in Section 6-1.

3.3.4 Effect of Temperatures on the Adipic Acid Degradation Rate

Three bench-scale runs were performed to evaluate the effects of temperature on the adipic acid degradation. These included a baseline run at 125°F (51.7°C), a high temperature run at 146°F (63.3°C), and a low temperature run at 93°F (33.9°C). Selected results from these runs are given in Table 3-12.

TABLE 3-12. EFFECT OF HOLD TANK TEMPERATURE ON THE ADIPIC ACID DEGRADATION RATE

Run #	Adipic Acid Degradation Rate Constant K_d, M^{-1}	Adipic Acid Degradation Rate, mg/g SO_2 Removed	Temperature, °F (°C)	Average Adipic Acid Concentration, ppm
R-17	0.52	20.0 ±7.7%	93 (33.9)	2449
R-13	1.39	45.4 ±3.3%	125 (51.7)	2159
R-25	2.33	81.7 ±1.9%	146 (63.3)	2246

Note: All three runs were performed at pH 4.6 - forced oxidation (100%).

These results show that the adipic acid degradation rate increases dramatically with temperature. This effect is illustrated in Figure 3-5 which is a plot of the adipic acid degradation rate constant K_d versus temperature.

The temperature dependence of many chemical reactions can be represented by the following empirical equation (4):

$$K = A \exp \{-E_a/RT\} \qquad \text{(Eq. 3-8)}$$

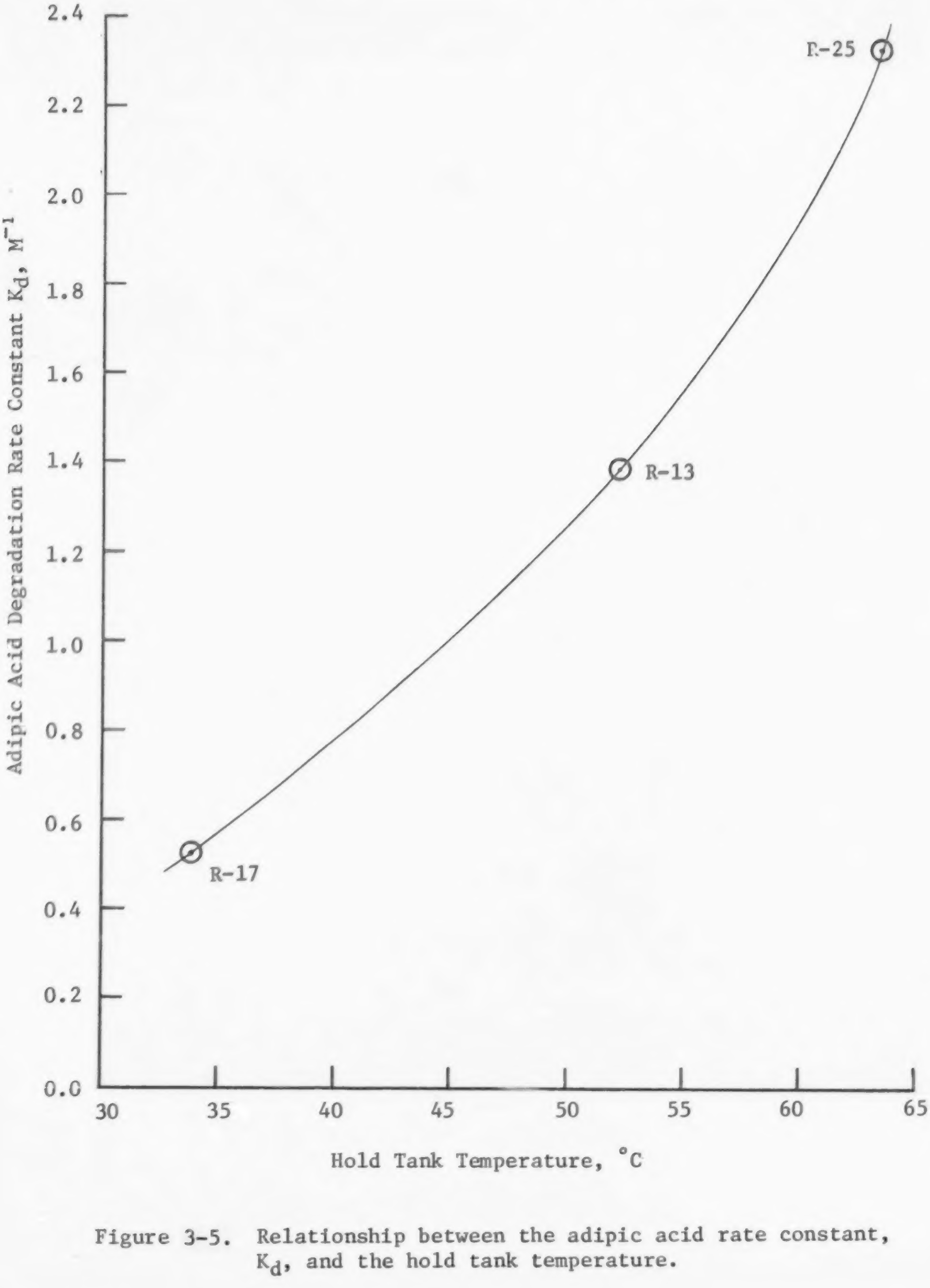

Figure 3-5. Relationship between the adipic acid rate constant, K_d, and the hold tank temperature.

where,

K = the chemical rate constant or an equivalent expression for the reaction rate,

A = a pre-exponential constant,

E_a = the Arrhenius activation energy,

R = the ideal gas constant, and

T = the absolute temperature.

This equation can be written in the logarithmic form:

$$\log_{10} K = \left(\frac{-E_a}{2.303R}\right) \frac{1}{T} + \log_{10} A \qquad \text{(Eq. 3-9)}$$

According to this equation, a plot of $\log_{10}$ K versus the reciprocal of the absolute temperature should be a line with a slope of ($-E_a/2.303$ R). A plot of this type is shown in Figure 3-6 in which the logarithm of the adipic acid rate constant, K_d, is plotted against the reciprocal of the absolute temperature. The use of K_d is appropriate here only because the percent oxidation and the average adipic acid concentration for the three runs are close. From the slope of the line shown in Figure 3-6, the Arrhenius activation energy was determined to be 10.6 Kcals/mole. This activation energy is typical for an organic reaction in which the rate is controlled by a chemical reaction rather than a physical process such as diffusion. The expression for the temperature dependence of K_d (only for this set of runs) is given below:

$$K_d,\ M^{-1} = 1.97 \times 10^7 \exp\left\{\frac{-5352}{T°K}\right\}$$

3.3.5 Effect of Sulfite Ion Concentration and Thiosulfate on the Adipic Acid Degradation Rate

The effects of changes in the equilibrium sulfite concentration and thiosulfate ion on the adipic acid degradation rate are discussed in this

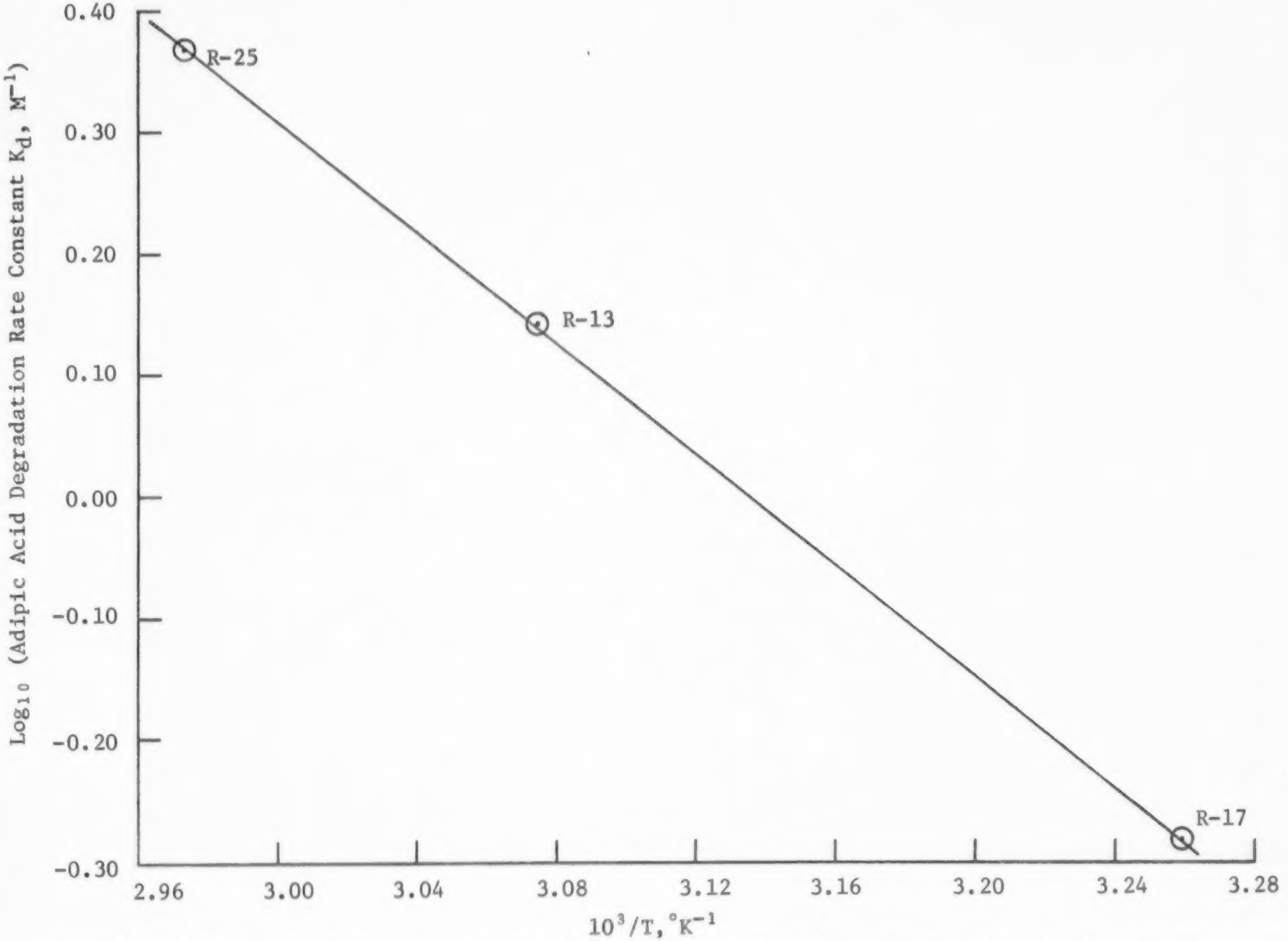

Figure 3-6. Plot of Log_{10} (K_d) versus reciprocal absolute temperature for the determination of the Arrhenius Activation Energy, E_a.

section. Selected results from runs illustrating the effects of these variables are given in Table 3-13 and 3-14.

One proposed mechanism of adipic acid degradation involves attack on the adipic acid molecule by a sulfur bearing free radical generated during sulfite oxidation. The equilibrium concentration of the radical is expected to be depressed with increasing concentrations of sulfite (5)(6). If this is the case, changes in the sulfite concentration should affect the adipic acid degradation rate.

In Section 3.3.1, the results of baseline testing were presented. The results indicated that pH and the sulfite concentration had no effect on the adipic acid degradation rate. However, these two variables are strongly dependent on one another. That is, a decrease in pH was always accompanied by an increase in the sulfite concentration over the pH range tested. For this reason, additional tests were performed in which the sulfite concentration was increased by the addition of Na^+ ions (as Na_2SO_4) to the hold tank. This allowed the comparison of adipic acid degradation rates from runs at the same pH but at different sulfite concentrations. Two such runs were performed. Run R-8 was a forced oxidation run at pH 5.5. In addition to Na_2SO_4 addition, the oxidation air rate was reduced to a level below that required for 100% oxidation in an effort to maximize the sulfite concentration. The resulting sulfite ion concentration was 2069 ppm compared to a concentration of 904 ppm observed in a similar baseline test (R-7). The average percent solids oxidation level was 81%. The adipic acid degradation rate for run R-8 was found to be somewhat below the value predicted from the baseline correlation (Section 3.3.1). However, the experimental uncertainty and the short run time (5 hours) make the significance of this comparison somewhat questionable. A more definitive answer is seen in the results of run R-21. Here, a fivefold increase in the sulfite concentration was achieved. The percent solids oxidation also increased over that seen in similar tests at "normal" sulfite ion concentrations. The degradation rate, however, was identical to that predicted from the baseline correlation for the adipic acid concentration and

TABLE 3-13. EFFECT OF INCREASED SULFITE CONCENTRATION[1] ON THE ADIPIC ACID DEGRADATION RATE

Run #	Adipic Acid Degradation Rate Constant K_d, M^{-1}	Adipic Acid Degradation Rate, mg/g SO_2 Removed	Predicted Adipic Acid Degradation Rate, mg/g SO_2 Removed[2]	Average Sulfite Ion Conc., ppm	Typical Sulfite Ion Conc., ppm	Run Conditions
R-8	0.59	73.8 ±20%	92.2	2069	904[3]	pH 5.5; forced oxidation High adipic acid conc; 5 hours
R-21	0.98	10.7 ±16%	10.7	2605	470[4]	pH 5.5; forced oxidation 22 hours

---

[1] Sulfite ion concentration increased over that of similar baseline tests by addition of Na^+ ions (as Na_2SO_4).

[2] Predicted adipic acid degradation from baseline data set correlation:

$$\text{adipic acid degradation rate, mg/g } SO_2 \text{ removed} = 0.00308 \text{ (adipic acid concentration, ppm)}^{0.5542} \text{ (percent oxidation)}^{1.185} \qquad \text{(Eq. 3-6)}$$

[3] Average sulfite concentration in Run R-7.

[4] Average sulfite concentrations in Runs R-1, R-11, R-20.

TABLE 3-14. EFFECT OF THIOSULFATE[1] ON THE ADIPIC ACID DEGRADATION RATE

Run #	Adipic Acid Degradation Rate Constant K_d, M^{-1}	Adipic Acid Degradation Rate, mg/g SO_2 Removed	Predicted Adipic Acid Degradation Rate, mg/g SO_2 Removed[2]	Average Percent Oxidation[3]	Run Conditions
R-28	1.26	1.7 ±123%	1.0	3.4	pH 5.1; forced oxidation [Thiosulfate, ave] = 251 ppm [$SO_3^=$, ave] = 1168 ppm; 19 hours

---

[1] Thiosulfate ion added as $Na_2S_2O_3$.

[2] Predicted adipic acid degradation from baseline data set correlation:

$$\text{adipic acid degradation rate, mg/g } SO_2 \text{ removed} = 0.00308 \text{ (adipic acid concentration, ppm)}^{0.5542} \text{ (percent oxidation)}^{1.185} \qquad \text{(Eq. 3-6)}$$

[3] Percent oxidation determined by direct analysis of $SO_4^=$. This procedure avoids large experimental uncertainty which would be present in a conventional determination of % oxidation by analysis for $SO_3^=$ and total sulfur.

percent oxidation used in the test. It would appear, therefore, that the sulfite concentration does not have a large impact on the adipic acid degradation rate mechanism.

Thiosulfate, a sulfite oxidation inhibitor, was added to the hold tank in run R-28. Even under forced oxidation conditions, the average percent oxidation was only 3.4 percent. The resulting degradation rate was extremely low. Even so, it was not significantly different from the value predicted from the baseline correlation developed in Section 3.3.1.

SECTION 4

COPRECIPITATION OF ADIPIC ACID IN SCRUBBER SOLIDS

There are at least three mechanisms for the loss of adipic acid from FGD scrubbers. These include:

- Chemical degradation of adipic acid,
- Physical loss of adipic acid in the liquid associated with the waste solids, and
- Physical loss of adipic acid coprecipitated or occluded with the waste solids.

Variables affecting chemical degradation have been discussed in Section 3. Physical loss of adipic acid in the liquid associated with the waste solids depends primarily on the degree to which waste solids are dewatered. This, in turn, is generally a function of percent oxidation since gypsum crystals dewater more completely than calcium sulfite crystals. The third loss mechanism, coprecipitation or occlusion of adipic acid with the waste solids, appears to be a strong function of the percent oxidation of the solids and the liquid phase adipic acid concentration.

Early bench-scale results indicated that losses of adipic acid in the waste solids were a significant fraction of total adipic acid losses. In order to further characterize this mechanism for adipic acid loss, two series of batch precipitation experiments were performed. The results of these tests are given in Section 4.1. Bench-scale data relating to coprecipitation of adipic acid in the solid waste stream is presented in Section 4.2. Data interpretation and the significance of adipic acid coprecipitation to total adipic acid losses are discussed in Section 4.3.

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4.1 BATCH PRECIPITATION TEST RESULTS

Two series of batch-precipitation tests were performed to determine factors involved in the coprecipitation of adipic acid in scrubber solids. The tests were designed to study:

- The mechanism for adipic acid coprecipitation (surface absorption versus occlusion or solid solution formation),
- The effect of liquid phase adipic acid concentration on adipic acid concentration in the scrubber solids, and
- The effect of the sulfite to sulfate ratio (oxidation fraction) on adipic acid coprecipitation.

In the first series of tests 1.0 M Na_2SO_3 and 1.0 M Na_2SO_4 were dripped into separate stirred solutions of 0.5 M $CaCl_2$ at 50°C. In tests with Na_2SO_3, a nitrogen blanket was maintained over the solutions and boiled DI water was used to prepare reagents. This procedure resulted in the precipitation of pure $CaSO_3 \cdot \frac{1}{2}H_2O$ or $CaSO_4 \cdot 2H_2O$ (gypsum) crystals. The pH was maintained at a constant value of either 4.6 or 5.5 by dropwise addition of hydrochloric acid. To test the surface absorption mechanism, about 3,000 ppm adipic acid was added to the slurries after precipitation had occurred. To test for occlusion/solid solution formation, about 3,000 ppm adipic acid was added before precipitation occurred. The amount of absorbed and occluded adipic acid was then determined by analysis of filtered and dried solids. The cake analysis was corrected for the amount of adipic acid calculated to have been associated with the adherent liquor in the wet cake based on weight percent solids in the cake and the measured concentration of adipic acid in the liquid phase. A summary of test results is given in Table 4-1.

TABLE 4-1. SUMMARY OF TEST RESULTS FOR ADDITION OF ADIPIC ACID BEFORE AND AFTER SOLIDS PRECIPITATION

	Solution pH			
	4.6		5.5	
Solids Phase	Before	After	Before	After
$CaSO_3 \cdot \frac{1}{2}H_2O$	15,500 ppm	<500 ppm	15,000 ppm	<500 ppm
$CaSO_4 \cdot 2H_2O$	640 ppm	<500 ppm	770 ppm	<500 ppm

Several conclusions can be made based on these results:

- The major mechanism for adipic acid coprecipitation is occlusion or solid solution formation and not surface absorption although absorption could still occur at the <500 ppm level,
- The extent of adipic acid coprecipitation is highly influenced by the oxidation fraction of the scrubber solids (sulfite versus sulfate), and
- The scrubber slurry pH does not significantly effect adipic acid coprecipitation (at least over the pH range tested).

The second series of batch precipitation tests was performed at pH 4.6 with various levels of adipic acid added before solids were precipitated and at intermediate levels of sulfate fraction in the product solids. The results of these tests and selected similar tests from the first test sequence are summarized in Table 4-2. The ratio of $[Ad]_s/[Ad]_\ell$ is plotted against the percent sulfate in the solids in Figure 4-1. Examination of the plot in Figure 4-1 as well as a simple inspection of the data shows that the concentration of adipic acid in the solids increases as the concentration of adipic acid in the slurry solution increases but decreases as the fraction of sulfate in the solids increases. The relationship between $[Ad]_s/[Ad]_\ell$ and solids sulfate fraction does not appear to be linear. This may be related to a change in mechanism from a sulfite-sulfate solid solution at low oxidation levels to pure gypsum formation at high oxidation levels.

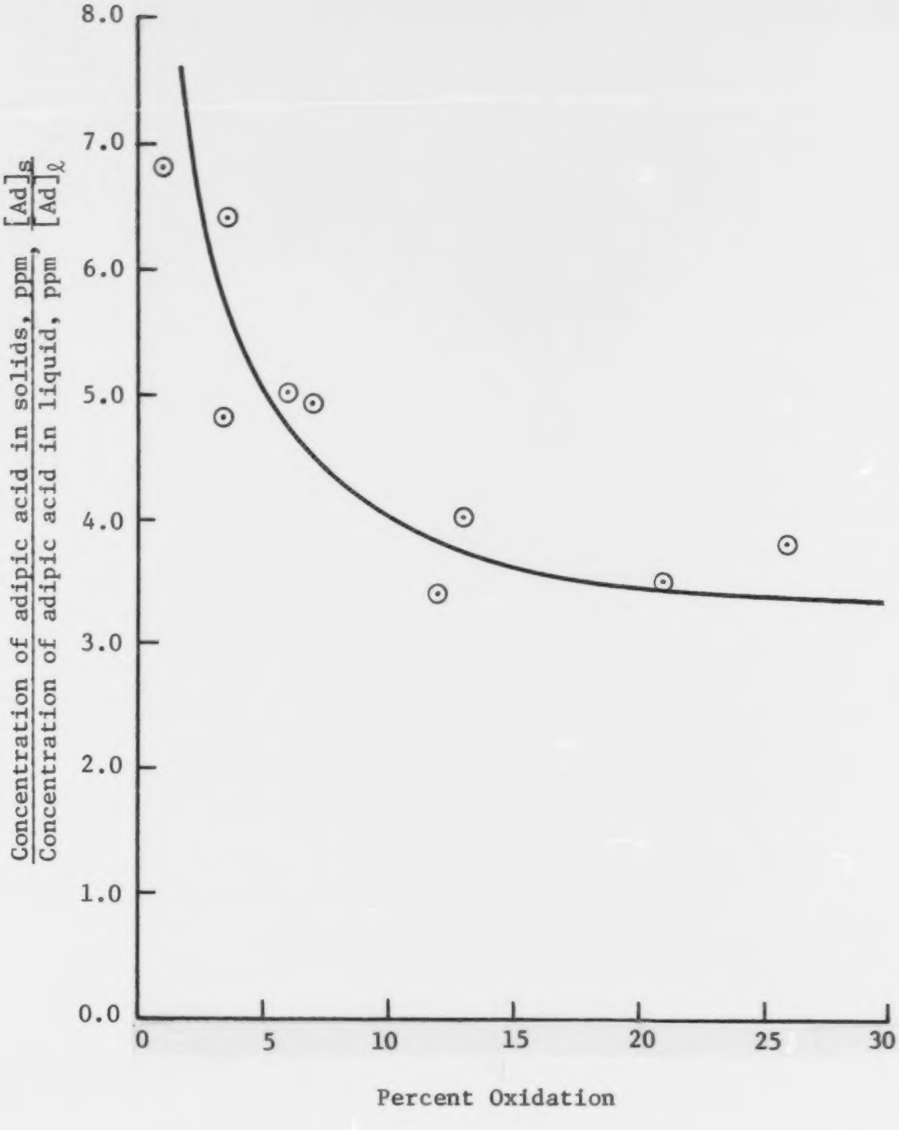

Figure 4-1. Normalized concentration of adipic acid in solids versus percent sulfate in solids

TABLE 4-2. SUMMARY OF TEST RESULTS FOR COPRECIPITATED ADIPIC ACID AT VARIOUS ADIPIC ACID CONCENTRATIONS AND SOLIDS OXIDATION LEVELS

% Oxidation In Solids	Adipic Acid Concentration In Solution, ppm	Adipic Acid Concentration In Solids, ppm	$[Ad]_s/[Ad]_\ell$
<1.0	2,400	16,200	6.8
3.4	3,100	15,000	4.8
3.7	2,300	14,800	6.4
6.0	9,300	46,500	5.0
7.0	5,800	28,400	4.9
12.0	9,100	31,300	3.4
13.0	6,600	26,600	4.0
21.0	3,500	12,300	3.5
26.0	3,600	13,800	3.8
100.0	3,100	640	0.2
100.0	3,500	770	0.2

The batch precipitation tests show the dramatic effects of adipic acid slurry concentration and solid phase percent oxidation on coprecipitation of adipic acid in scrubber solids. Real world scrubbers would probably never operate at adipic acid concentrations as high as those tested and would also not likely ever produce pure phase calcium sulfite hemihydrate. Therefore, the magnitude of the results observed is somewhat a product of the laboratory test conditions. The results do, however, establish the potential importance of adipic acid coprecipitation and, hence, the need for analysis of scrubber solids for adipic acid when determining adipic acid chemical degradation rates by a mass balance calculation approach.

4.2 ADIPIC ACID COPRECIPITATION IN THE BENCH-SCALE SAMPLES

The batch-tests described in the previous section illustrate the potential importance of adipic acid coprecipitation and the dependence of this phenomenon on the percent oxidation in the solids. The numerical results, however, are not necessarily indicative of what might be expected to occur during actual FGD system operation since the conditions under which precipitation occurs in actual systems differ greatly from those of the batch tests. Conversely, the conditions under which the bench-scale system solids were formed are quite similar to those of actual FGD systems. These similarities include continuous solids precipitation in the presence of sulfite oxidation, a similar liquid phase chemical composition, and long solid phase residence times. Thus, results obtained from the bench-scale tests should be suitable for predicting the degree of adipic acid coprecipitation during full-scale FGD operation.

Results from the bench-scale data base relating to coprecipitation of adipic acid are shown in Figure 4-2. This figure shows the ratio of solid and liquid phase adipic acid concentrations versus percent oxidation in the solids. Note that the data for Figure 4-2 are listed in Table 3-3 in Section 3.

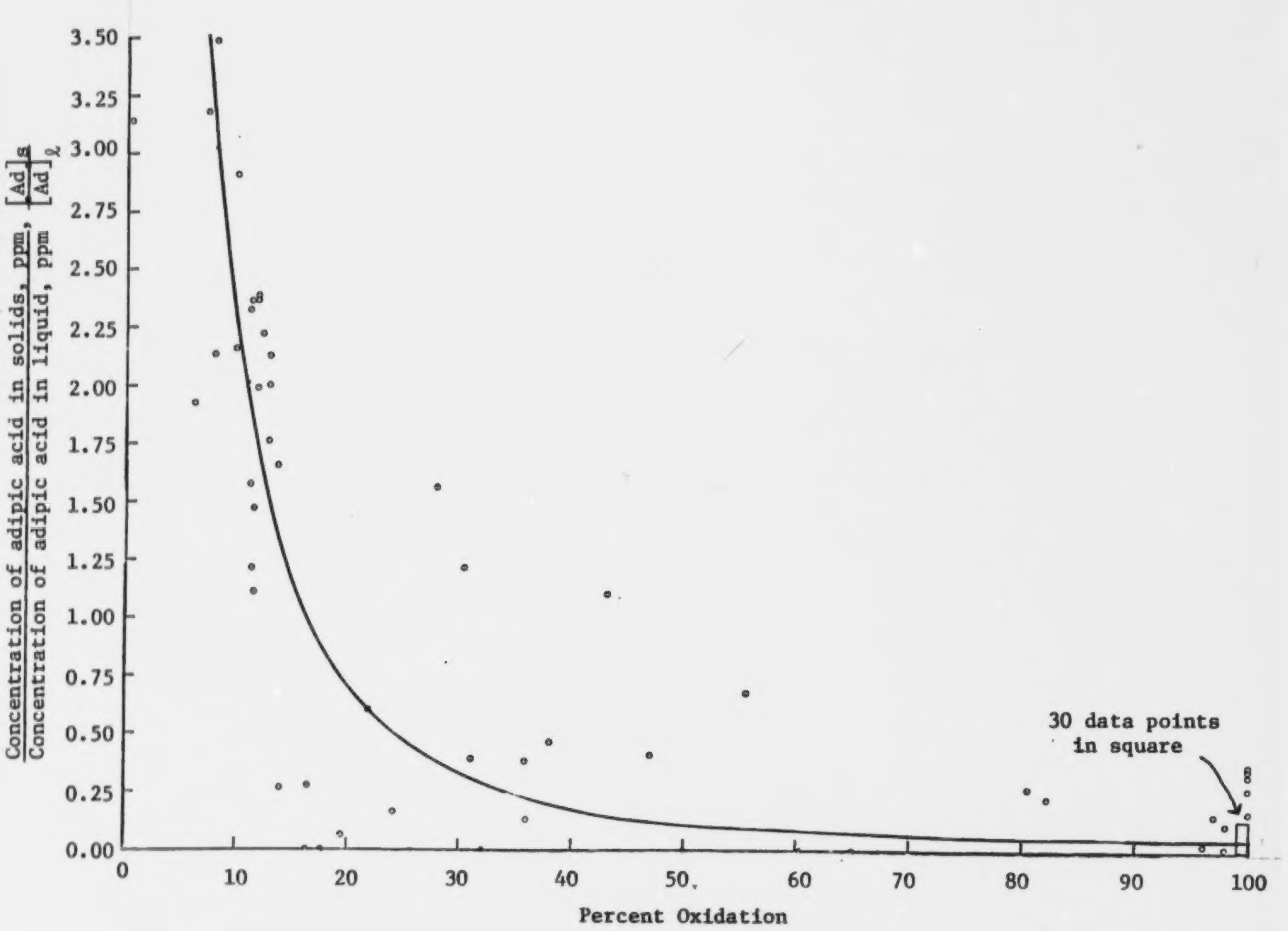

Figure 4-2. Relationship of adipic acid content of bench-scale solids to percent oxidation.

The results given in Figure 4-2 show that the amount of coprecipitated adipic acid is strongly related to the percent oxidation of the solids and the concentration of adipic acid in the liquid phase. Note the similarity between the shape of the curve in Figure 4-2 with that given for the batch-tests in Figure 4-1. The concentration of adipic acid in the solids refers only to the adipic acid actually coprecipitated or occluded in the solids. That is, adipic acid contributed from the liquid associated with the filter cake is not included.

The results of previous studies at Radian (11) have demonstrated that the precipitated solids exist as a solid solution at low levels of percent oxidation. The composition of this solid solution has been proposed to be:

$$[(1-x)\ CaSO_3 + x\ CaSO_4]\cdot\tfrac{1}{2}H_2O \qquad \text{(Eq. 4-1)}$$

where $0 \leqslant x \leqslant 0.16$.

The physical interpretation of these results is as follows. At low levels of percent sulfite oxidation, the scrubber solution is subsaturated with respect to gypsum ($CaSO_4\cdot 2H_2O$). Even so, $CaSO_4$ can precipitate within the calcium sulfite matrix as a solid solution. At roughly 16 percent oxidation, saturation with respect to gypsum is achieved and pure phase gypsum begins to precipitate. Thus, at oxidation levels greater than 16 percent, the solids are composed of both the calcium sulfite/sulfate solid solution and gypsum. As the level of oxidation increases, the fraction of solids which exist as the solid solution decreases until, at 100 percent oxidation, no sulfite solids are formed. The composition of solid solution remains at that given in Equation 4-1 regardless of the overall oxidation level at which the solid solution is formed. This indicates that the sulfite crystal structure is essentially saturated with respect to $CaSO_4$.

The results of the batch tests and the bench-scale results show that large quantities of adipic acid can be coprecipitated or occluded within the crystal structure of the solid solution. By contrast, almost no adipic acid is coprecipitated or occluded within the gypsum crystal structure. Considerable data scatter, however, is observed in Figure 4-2 for intermediate levels of oxidation, particularly in the range of 15 to 50 percent oxidation. Some high values of adipic acid in the solids were observed within this region. This would suggest that the solid solution is capable of containing coprecipitated adipic acid even when pure phase gypsum is precipitating. Perhaps there is a competition between adipic acid and $CaSO_4$ for the available space within the calcium sulfite crystal structure. In this case, the relative concentrations of adipic acid and coprecipitated $CaSO_4$ might well be determined by factors other than percent oxidation. These factors might include the concentrations and relative saturations of the species involved, the pH, temperature, and weight percent solids of the hold tank, the precipitation rate, or a variety of other possible variables.

A limited amount of data related to the coprecipitation of adipic acid is available from the full-scale adipic acid demonstration project at City Utilities Southwest Power Station in Springfield, MO (8). These results are given in Figure 4-3. This figure shows the Springfield results superimposed on the relationship given in Figure 4-2 for the bench-scale results. It would appear that the concentrations of adipic acid found in the solids at Springfield are close to what would be predicted, based on the bench-scale results.

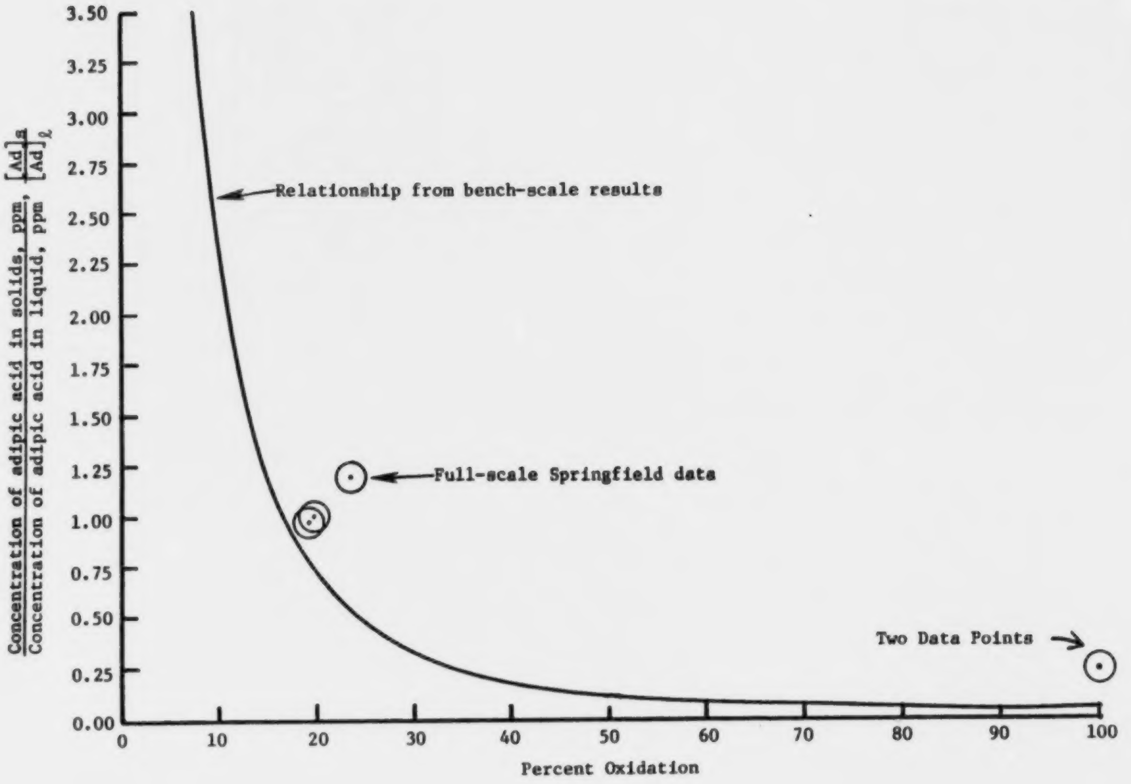

Figure 4-3. Comparison of the adipic acid content of solids from the full-scale demonstration program at Springfield, MO to the relationship developed from bench-scale testing.

SECTION 5

ANALYSIS OF BENCH-SCALE SAMPLES FOR ADIPIC ACID AND ADIPIC ACID DEGRADATION PRODUCTS

The analytical task for the study of adipic acid degradation addresses two problems:

1) The development and optimization of methods for determining adipic acid and its potential degradation products, and

2) The identification and quantitation of those degradation products in samples from adipic acid enhanced scrubber systems.

Previous work by Radian and other investigators strongly suggests the possibility of adipic acid degradation by a free radical, conjugated oxidative decarboxylation mechanism (6)(12). Such a mechanism provides for the generation of alphatic mono- and dicarboxylic acids (C_1-C_5), as well as C_1-C_4 aliphatic hydrocarbons and CO_2 (Figure 5-1). There is also the potential for forming higher order (>C_6) organics and other classes of compounds.

5.1 ANALYTICAL STRATEGY

Based on the above theory, as well as prior analytical efforts, an analysis scheme was developed for assessing the levels of adipic acid and probable degradation products in solid, liquid, and gas scrubber streams (6)(13). The accompanying flow chart (Figure 5-2) outlines the analytical approach employed.

Solid, liquid, and gas phase scrubber samples were taken in order to monitor the production of degradation products and the loss of adipic acid from the bench-scale system. A portion of the scrubber slurry was routinely

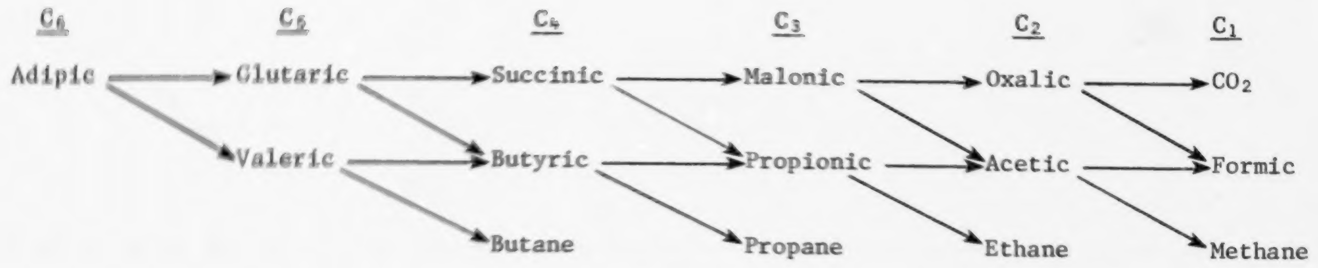
C_6
C_5
C_4
C_3
C_2
C_1
Adipic
Glutaric
Succinic
Malonic
Oxalic
CO_2
Valeric
Butyric
Propionic
Acetic
Formic
Butane
Propane
Ethane
Methane

Figure 5-1. Conjugated oxidative decarboxylation of adipic acid.

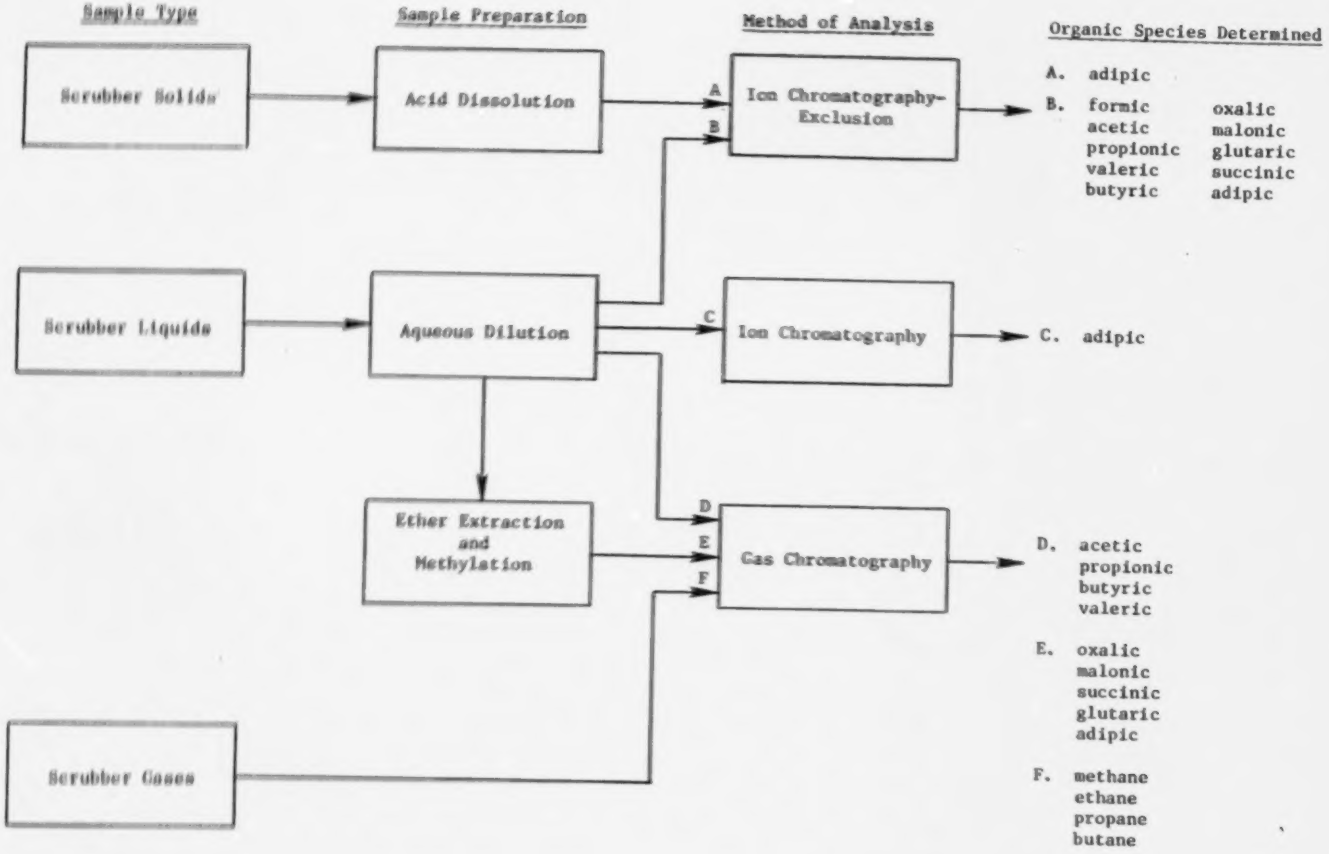
Sample Type
Sample Preparation
Method of Analysis
Organic Species Determined
Scrubber Solids
Acid Dissolution
A
B
Ion Chromatography-Exclusion
A. adipic
B. formic acetic propionic valeric butyric oxalic malonic glutaric succinic adipic
Scrubber Liquids
Aqueous Dilution
C
Ion Chromatography
C. adipic
Ether Extraction and Methylation
D
E
F
Gas Chromatography
D. acetic propionic butyric valeric
E. oxalic malonic succinic glutaric adipic
F. methane ethane propane butane
Scrubber Gases

Figure 5-2. Analysis scheme for adipic acid and potential degradation products.

collected during each test run and filtered to provide separate solid and liquid fractions. The solids were screened for the presence of coprecipitated or occluded adipic acid. The filtrate was examined for adipic acid, as well as adipic degradation products. In a few instances, grab samples of scrubber gases were taken from the scrubber flue gas outlet in an effort to assess the production of low molecular weight hydrocarbons.

The preparation of slurry samples depended partly upon the species of interest and the method of analysis to be employed. Solids samples were dissolved in approximately 0.02 N HCl for subsequent analysis by ion chromatography-exclusion (ICE). Filtrate samples were diluted and analyzed for adipic acid by ion chromatography (IC) and ion chromatography-exclusion (ICE). With gas chromatography (GC), the volatile monobasic carboxylic acids could be determined by direct injection of the aqueous samples. Extraction of the filtrates with diethyl ether followed by derivitization with diazomethane was necessary for the determination of dibasic carboxylic acids.

Analytical techniques were selected and developed to provide different, as well as overlapping, information with regard to the organic species present in the scrubber samples.

Ion chromatography (IC) provided a relatively rapid estimate of adipic acid concentration, as well as the concentrations of inorganic ions such as sulfate and chloride. IC analysis is simple, reproducible, and had been used previously with numerous bench-scale and pilot plant samples. Unfortunately, IC does not adequately resolve mixtures of multiple carboxylic acids.

Ion chromatography-exclusion (ICE) was employed as an alternative to normal IC analysis. ICE takes advantage of the acid properties of the various carboxylic compounds and provides separation based on differences in pK_a values and ion size. Testing has shown that many of the carboxylic acids of interest can be separated, identified, and quantitated using ICE. A major advantage of ICE is that the anions of strong inorganic acids (e.g.,

SO_4^{-2}) elute before the weaker organic acids. Also, the eluent used in ICE chromatography is HCl. This allows an HCl dissolution of the scrubber solids to be analyzed without chloride interference.

Gas chromatography was, of course, the method of choice for the volatile alkanes, but it had previously served only a limited role in the determination of the carboxylic acids. Considerable effort was invested in adapting GC to the needs of this project and to developing a viable technique for the speciation of mixtures of organic acids. Based on boiling points, the potential (C_2-C_5) carboxylic acid degradation products of adipic acid form two distinct classes of compounds:

1) Acids which boil below 200°C, including acetic, propionic, butyric, and valeric.
2) Acids which decompose upon heating or boil above 200°C, including oxalic, malonic, succinic, glutaric, and adipic.

In order to apply GC to mixtures containing both classes of acids, it was necessary to use two separate methodologies. The monobasic acids are volatile enough to be determined directly in aqueous samples, while the dibasic acids must be derivatized.

5.2 GAS CHROMATOGRAPHY TECHNIQUES

5.2.1 Low Molecular Weight Hydrocarbons

The development of an analysis for C_1-C_4 n-paraffins involved choosing an appropriate sampling procedure, selecting an analytical technique, and characterizing the technique.

The two most widely used approaches to sampling for low molecular weight hydrocarbons are grab sampling or the use of solid sorbent traps. Several types of sorbents have been tested in the past, including: activated carbon, silica gel, and Poropak-Q (6). In general, the use of sorbents has been plagued by problems such as variable trapping efficiencies, imcomplete desorption, and sample contamination. Grab sampling provides a simple solution to these problems.

The grab samples were taken from a port near the flue gas outlet of the bench-scale scrubber. A 5-cm long hypodermic needle, attached to a 100-cc gas sampling syringe, was inserted directly into the scrubber port. The syringe was flushed with two volumes of scrubber gas, then the gas sample was rapidly drawn into the syringe. The syringe was sealed by closing the intake valve to prevent sample loss or contamination. This sample contained sufficient gas for several GC analyses.

Analysis for methane, ethane, propane, and butane was carried out with an Antek Model 460 gas chromatograph equipped with a flame ionization detector (FID). The following experimental conditions were employed:

- Column: Poropak-Q (6', stainless steel)
- Gases: N_2 (carrier) = 30 ml/min
  H_2 (FID) = 32 ml/min
  Air (FID) - 167 ml/min
- Temperatures: Oven = 70-170°C @ 10°/min
  Detector = 250°C
- Electrometer: Range = 10^{-11} to 10^{-12}A
  Attenuation = 1
- Sample size: 2 ml, using a fixed volume stainless steel sample loop

For qualitative and quantitative purposes, unknown samples were compared to a standard gas mixture:

- methane - 15.1 ±1.5 ppmv
- ethane - 14.6 ±1.5 ppmv
- propane - 15.6 ±1.6 ppmv
- butane - 15.2 ±1.5 ppmv

Table 5-1 summarizes the analytical results obtained using the standard hydrocarbon gas mixture and Figure 5-3 shows a typical chromatogram.

TABLE 5-1. SUMMARY OF ANALYTICAL PARAMETERS FOR C_1-C_4 ALIPHATIC HYDROCARBONS DETERMINED BY GC

Hydrocarbon	Retention[1] Time (min)	Relative[2] Retention Time	Response[1] (Area/ppmv)	Relative[2] Response	Estimated Detection Limit (ppmv)
methane	0.53 ±0.1	0.09	3340 ±220	0.25	1.0
ethane	1.24 ±.02	0.21	6810 ±190	0.52	0.5
propane	3.00 ±.03	0.50	9480 ±320	0.72	0.3
n-butane	6.00 ±.04	1.0	13200 ±440	1.00	0.2

[1] Uncertainties represent standard deviation for six determinations made over a period of seven days.

[2] Relative to n-butane.

The species of interest are obviously well separated and all peaks are symmetrical. Retention times are very reproducible and provide an excellent basis for qualitative identification of species in unknown samples. The absolute response is also reasonably consistent, with uncertainties of only 3-7%. As illustrated in Figure 5-4, relative response is in good agreement with theoretical expectations. There is an excellent linear correlation between response and the number of carbon atoms per molecule:

correlation coefficient = 0.999
slope = 0.247
y-intercept = 0.004

Detector noise effectively limits the minimum detectable quantity of methane to about 1 ppmv; however, the longer chain molecules have somewhat lower detection limits.

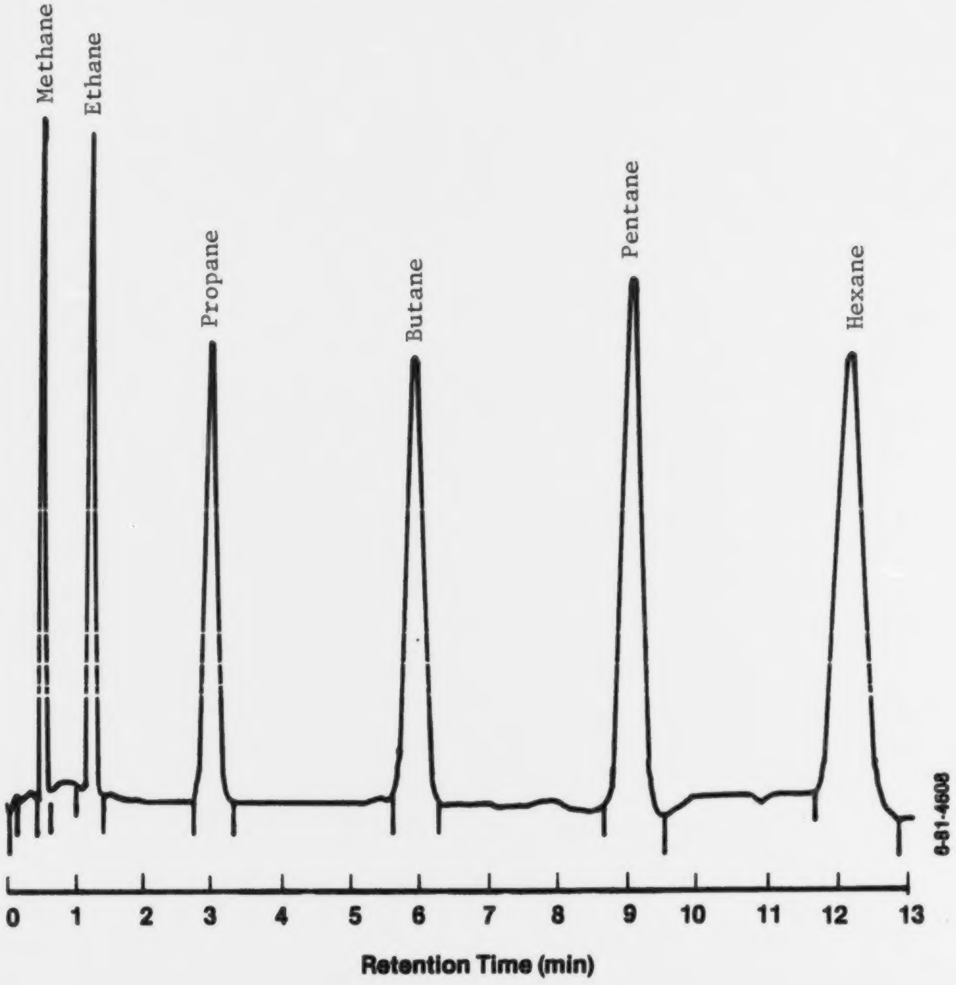

Figure 5-3. Gas chromatogram of a standard hydrocarbon gas mixture containing 15.1 ppmv methane, 14.6 ppmv ethane, 15.6 ppmv propane, 15.2 ppmv butane, 15.6 ppmv pentane, and 15.9 ppmv hexane.

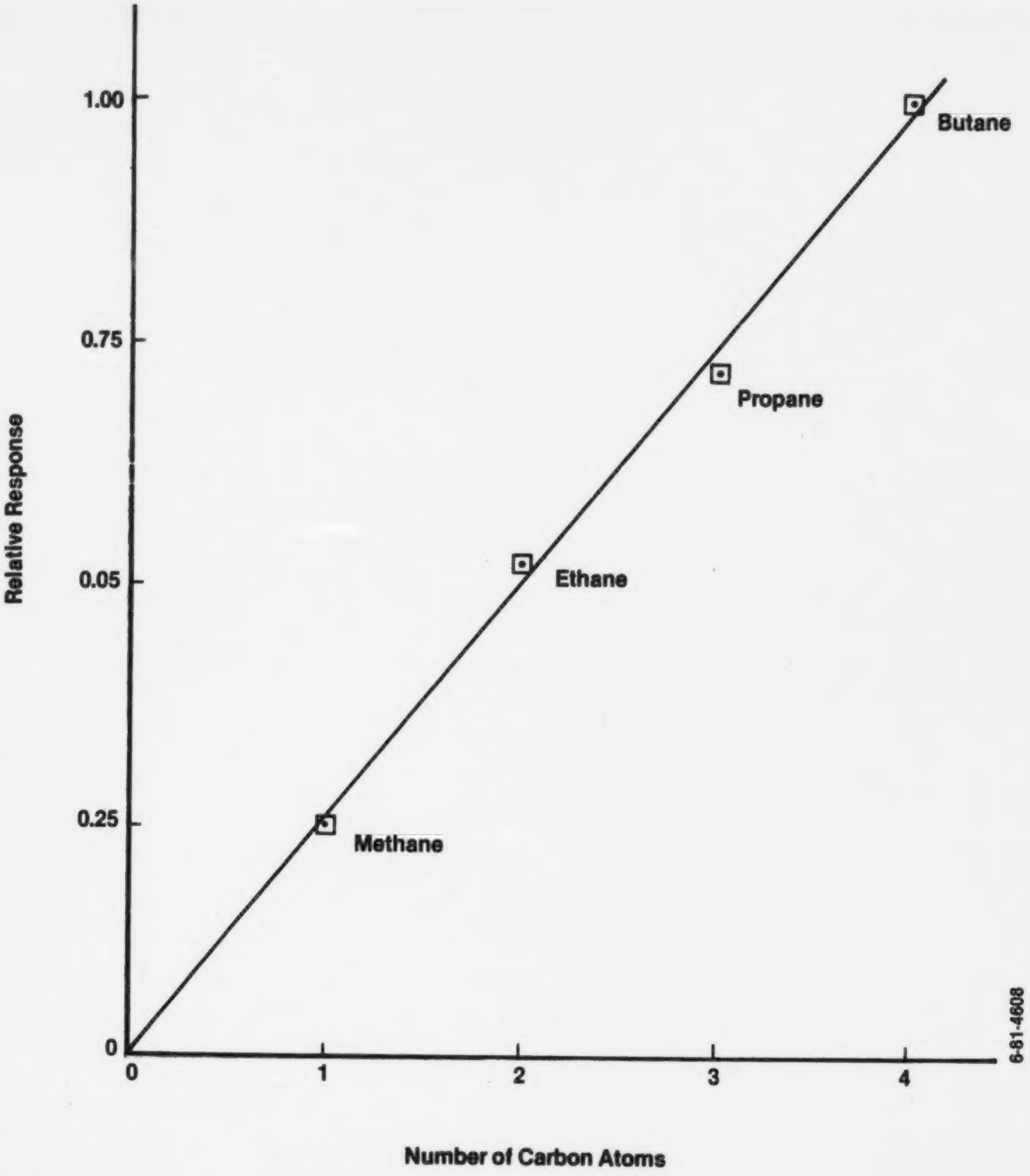

Figure 5-4. Plot of response versus number of carbon atoms for the GC determination of C_1-C_4 n-paraffins.

5.2.2 Monoprotic Carboxylic Acids

Aqueous samples containing mixtures of acetic, propionic, butyric, and valeric acids were acidified to pH 1 with concentrated HCl and analyzed on a Tracor Model 560 gas chromatograph equipped with dual flame ionization detectors. Chromatograms were acquired and processed by either a Varian VISTA® data system or a Hewlett Packard Model 3390A reporting integrator. As illustrated in Figure 5-5, the following experimental conditions provide rapid and efficient separation of the monobasic carboxylic acids:

- Column: Tenax, 60-80 mesh (6', glass)
- Gases: N_2 (carrier) = 20 ml/min
  H_2 (FID) = 42 ml/min
  Air (FID) = 600 ml/min
- Temperatures: Oven = 150-250°C @ 10°/min, with a 10 min initial hold
  Detector = 250°C

The oven temperature was programmed to permit elution of all four monoprotic acids under isothermal conditions (during the first 10 min.). Figure 5-6 demonstrates the excellent linear correlation that is obtained between the retention times and boiling points. Such a relationship can be extremely helpful when attempting to identify unknown peaks and it is strong evidence that the behavior of the GC technique corresponds to theoretical expectations.

Table 5-2 summarizes the analytical results observed with aqueous standards containing varying amounts of the four monofunctional carboxylic acids of interest:

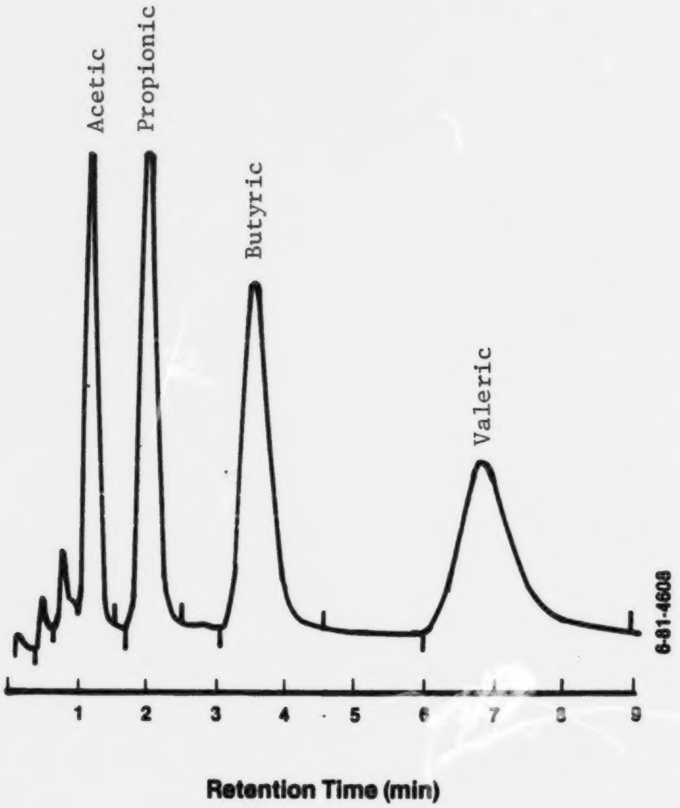

Figure 5-5. Gas chromatogram of an aqueous standard containing 104.9 ppm acetic acid, 99.3 ppm propionic acid, 96.4 ppm butyric acid, and 93.9 ppm valeric acid.

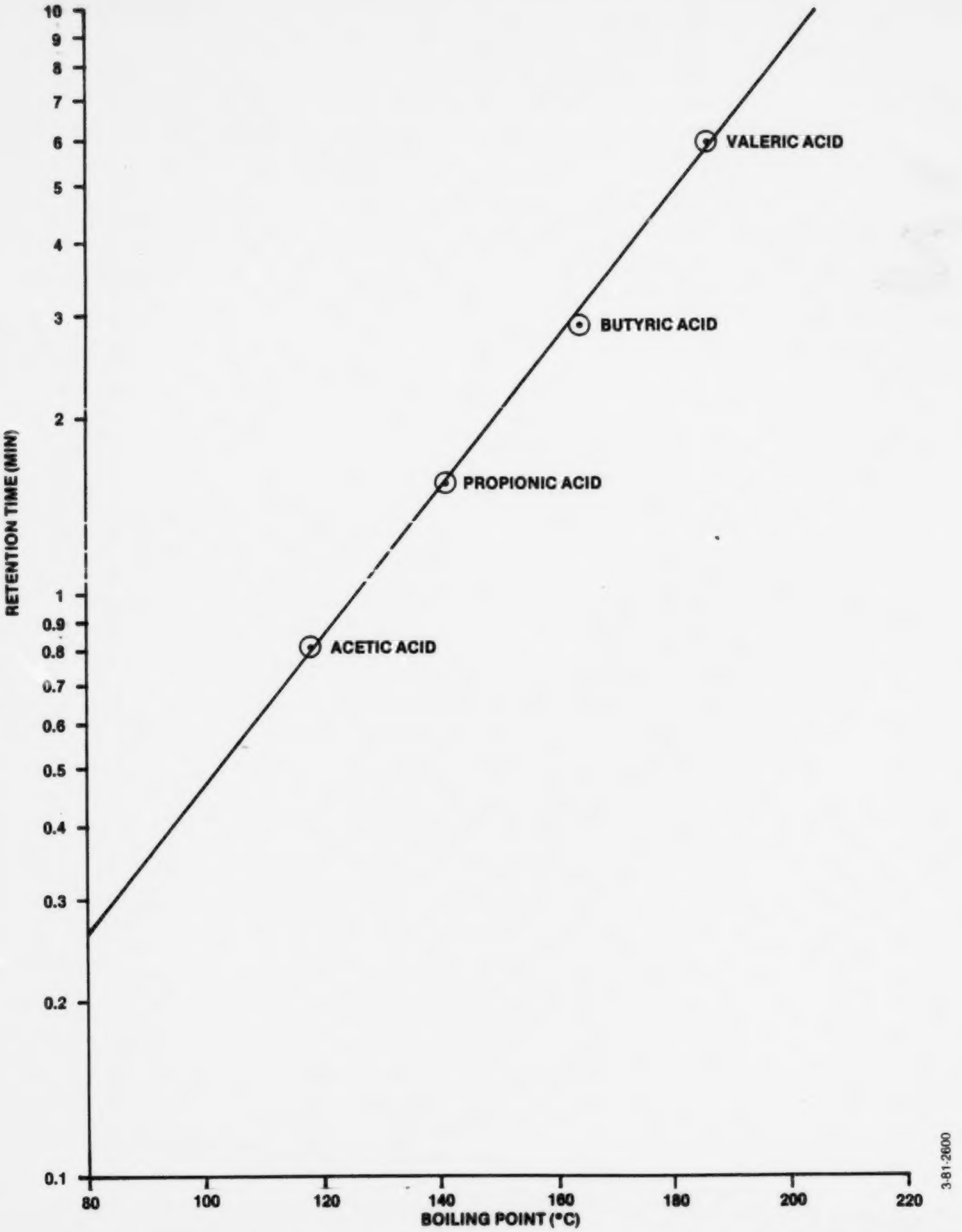

Figure 5-6. Correlation between retention times and boiling points for monobasic carboxylic acids determined isothermally at 150°C using a Tenax column.

TABLE 5-2. SUMMARY OF TYPICAL ANALYTICAL RESULTS FOR MONOBASIC CARBOXYLIC ACIDS DETERMINED DIRECTLY IN STANDARD AQUEOUS SAMPLES BY GC

Acid	Retention[1] Time (min)	Response[1] (Area/ng)	Minimum Detection Limit (ppm)[2]
Acetic	1.09 ±0.14	318 ±67	1.6
Propionic	1.91 ±0.09	415 ±36	1.2
Butyric	3.46 ±0.04	494 ±26	1.0
Valeric	6.78 ±0.09	548 ±67	0.9

[1] Uncertainties represent standard deviations for 7 analyses.

[2] Based on a 2 μL sample aliquot.

5.2.3 Diprotic Carboxylic Acids

The dicarboxylic acids, oxalic, malonic, succinic, glutaric, and adipic, were derivatized prior to GC analysis to provide more volatile compounds. Dimethyl esters were produced in a three step process:

1) The aqueous solution of dicarboxylic acids was adjusted to pH 1 to insure complete protonation of the acids.

2) The carboxylic acids were removed from the aqueous phase by extraction into diethyl ether.

3) The ether extracts were then reacted with diazomethane to form the methyl esters of the carboxylic acids.

The following detailed derivatization procedure was developed:

a) Mix the sample well, take a 100-ml aliquot and pipet into a 250-ml beaker.

b) Adjust the pH to 1 with concentrated HCl.

c) Transfer the sample to a 500-ml separatory funnel.

d) Rinse the beaker with 150 ml of unpreserved diethyl ether (Et_2O) and add the rinse to the separatory funnel.

e) Vigorously shake the separatory funnel for three (3) minutes, venting periodically to relieve pressure.

f) Let the separatory funnel stand and allow the ether and water layers to separate completely.

g) Drain the bottom (aqueous) layer back into the original 250-ml beaker.

h) Drain the ether layer into a 1000-ml Ehrlenmeyer flask and stopper the flask.

i) Repeat steps c-h four more times.

j) After the final extraction, rinse the separatory funnel with 25 ml of Et_2O and add the rinse to the other extract.

k) Discard the aqueous portion.

l) Add sufficient anhydrous Na_2SO_4 to the ether extract to remove any water.

m) Transfer the ether extract to a 1000-ml Kuderna-Danish evaporative concentrator (K-D) equipped with a 10-ml receiver and a boiling chip.

n) Rinse the Ehrlenmeyer flask with 25 ml of Et_2O and add to the K-D.

o) Wet the Snyder column on the K-D with a few (5) milliliters of Et_2O and place the K-D on a steam bath.

p) Reduce the volume of the ether extract to ≃50 ml, remove the K-D from the steam bath, and allow to cool.

q) Transfer the ether extract to a 100-ml volumetric flask.

r) Rinse the K-D and the receiver with Et_2O, add the rinse to the volumetric, makeup to volume with Et_2O, and mix thoroughly.

s) Take a 1-ml aliquot of the ether extract from the volumetric flask and pipet into a 5-ml hypovial. Make a mark on the side of the hypovial to mark the height of the solution in the vial.

t) Add ≈3 ml of 1% diazomethane to the hypovial and place in a covered container in an exhaust hood. (The sample should be shielded from light as much as possible.)

u) After 3-4 hours the extract should be colorless and the methylation reaction should be complete.

v) The final volume of solution in the hypovial should be 1 ml. If concentration is necessary, use a gentle stream of nitrogen to evaporate the ether to the 1-ml mark on the hypovial.

w) Crimp-seal the hypovial with a Teflon-lined septum and refrigerate until analyzed.

The derivatization procedure introduces two major uncertainties into the analysis of the dicarboxylic acids:

1) The extraction efficiencies for the various acids were unknown, and

2) The methylation efficiencies were also unknown.

Without a basic knowledge of the extent and variability of these processes, it would be impossible to relate the quantity of esterified acid found in the ether extract to the concentration of the acid in the original aqueous sample.

Methylation efficiencies were investigated by dissolving known amounts of the acids in diethyl ether, subjecting these ether standards to the methylation procedure, and comparing the resultant dimethyl ester concentrations with the initial acid concentrations. It was found that all of the dicarboxylic acids undergo conversion to their respective dimethyl esters with 100 ±2% efficiency. Diazomethane is a strong methylating agent, so the efficiency of this process was not surprising.

Extraction efficiencies were examined by carrying aqueous acid standards through the entire extraction and methylation procedure and measuring the amount of acid recovered. Table 5-3 summarizes the results obtained with different initial concentrations of acids.

TABLE 5-3. SUMMARY OF EFFICIENCIES FOR EXTRACTING DICARBOXYLIC ACIDS FROM WATER INTO DIETHYL ETHER

Acid	Initial Concentrations Aqueous Acid (ppm)	Average Extraction Efficiency (%)[1,2]
Adipic	100, 500, 1000	87 ±3
Glutaric	50, 100	64 ±2
Succinic	50, 100	47 ±6
Malonic	100, 200	51 ±3

[1] Uncertainties represent average standard deviation for determinations at all concentration ranges.

[2] Extraction efficiency for five-1.5:1 ether to water extraction at pH 1.

Extraction efficiencies were found to vary significantly from acid to acid, but they were not concentration dependent for a given acid at the levels that were investigated.

GC analysis of the esterfied acids was carried out under conditions similar to those used for the monoprotic acids, only the oven temperature program was modified:

- Column: Tenax, 60-80 mesh (6', glass)
- Gases: N_2 (carrier) = 20 ml/min
  H_2 (FID) = 42 ml/min
  Air (FID) = 600 ml/min
- Temperatures: Detector = 250°C
  Oven = 150-200°C @ 10°/min, with a 5 min initial hold

Figure 5-7 presents a typical chromatogram for a standard mixture of adipate, glutarate, succinate, malonate, and oxalate esters. All species are well separated from the solvent (ether) peak and from each other. As can be seen, all five of the esters elute in approximately 15 minutes. Table 5-4

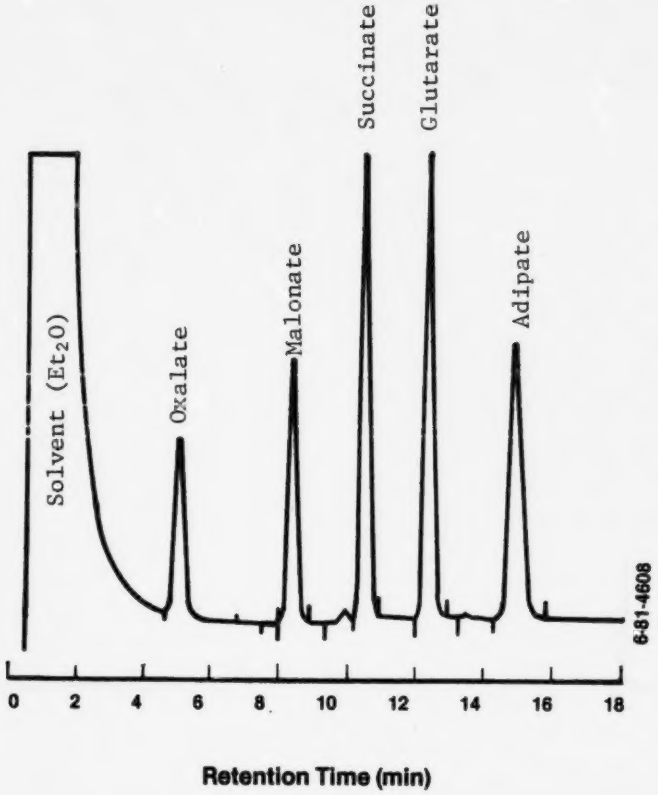

Figure 5-7. Gas chromatogram of an ether standard containing the dimethyl esters of five carboxylic acids: 95.5 ppm oxalate, 91.5 ppm malonate, 91.2 ppm succinate, 86.9 ppm glutarate, and 83.2 ppm adipate.

summarizes the behavior of the dimethyl esters typically observed with this GC technique.

TABLE 5-4. SUMMARY OF TYPICAL ANALYTICAL RESULTS FOR DICARBOXYLIC ACIDS DETERMINED AS DIMETHYL ESTERS BY GC

Dimethyl Ester	Retention Time (min)[1]	Response (Area/ng)[1]	Minimum Detection Limit (ppm)[2]
Adipate	14.80 ±.12	2767 ±130	1.7
Glutarate	12.23 ±.08	2962 ±246	1.6
Succinate	10.36 ±.06	2516 ±111	1.9
Malonate	8.21 ±.08	1420 ±38	3.4
Oxalate	4.84 ±.12	1090 ±16	4.4

[1] Uncertainties represent standard deviation for 4 analyses.

[2] Based on a 2 μL sample aliquot.

As with the monoprotic acids, retention times are very reproducible (i.e., better than ±2.5%).

5.3 ION CHROMATOGRAPHY TECHNIQUES

Ion chromatography (IC) and ion chromatography-exclusion (ICE) were applied to the bench-scale samples. Conventional IC has been used extensively in the past by Radian to analyze for adipic acid, as well as inorganic anions such as chloride and sulfate. ICE was included in this study because of its unique ability to separate strong inorganic acids and their salts from weaker organic acids. Also, ICE provides separation of the carboxylic acids in a very low conductance background, which extends the detection limits to <1 ppm.

Both methods combine the techniques of ion exchange, liquid chromatography, and conductometric detection for the determination of aqueous ionic species. A sample is injected by means of a 0.1 ml sample loop and is eluted through a system of two ion exchange columns and a conductivity cell. The first column separates the ions in the sample. Each different ion has a characteristic retention time on the column for a given set of conditions. The second column removes the eluent carrier ions thus minimizing the background conductivity of the eluent. Finally, a conductivity cell is used to determine the concentration of ions in the sample. By comparing the sample ions retention time to known standards, specific ions are identified.

5.3.1 IC Analysis

The IC method employed in this project was essentially the same as that which compared favorably with other methods in a round robin study conducted by the Research Triangle Institute in 1980 (14). A Dionex Model 14 ion chromatograph was employed under the following experimental conditions:

Instrument Settings:

- Linear Mode
- 10 μmhos full-scale
- Offset (coarse) ≈200
- Pump setting at 30-40%

Anion Columns:

- Pre-column (3 x 50 mm or 3 x 150 mm)
- Separator column (4 x 250 mm high resolution column)
- Suppressor column (6 x 250 mm)

Eluent Solution:

- 65-75% of standard eluent concentration (0.003 M $NaHCO_3$ + 0.0024 Na_2CO_3). Concentration adjusted in order to achieve maximum adipic acid separation from Cl^- and $SO_4^=$.

Because of the typically large ratio of inorganic anions (Cl^- and $SO_4^=$) to adipic acid, resolution of the baseline and adipic peak can be a problem. In this study, there was generally no problem with resolving the adipic acid in filtrate samples (Figure 5-8).

In some cases, the mono- and dicarboxylic acid degradation products can be detected by IC. Table 5-5 shows the retention times and response factors for these materials. The retention times and response factors of other materials commonly observed in scrubber samples are also included in Table 5-5.

5.3.2 ICE Analysis

Although IC and ICE analyses were both performed on a Dionex Model 14 ion chromatograph, ICE was carried out under significantly different experimental conditions:

Instrument Settings:

- Linear mode
- 10 μmhos full-scale
- Offset (coarse) ≃50
- Pump setting 15-20%

Columns:

- Normal ICE anion separator (9 x 200 mm)
- ICE anion suppressor

Eluent

- 0.001 M HCl
- Flow rate 0.7 ml/min @ ≃400 psi

The above parameters were optimized using standard mixtures of adipic acid and its possible adipic degradation products. Mixtures containing as many as ten different carboxylic acids were run (Figure 5-9), but due to overlapping retention times, only seven of the ten acids were successfully

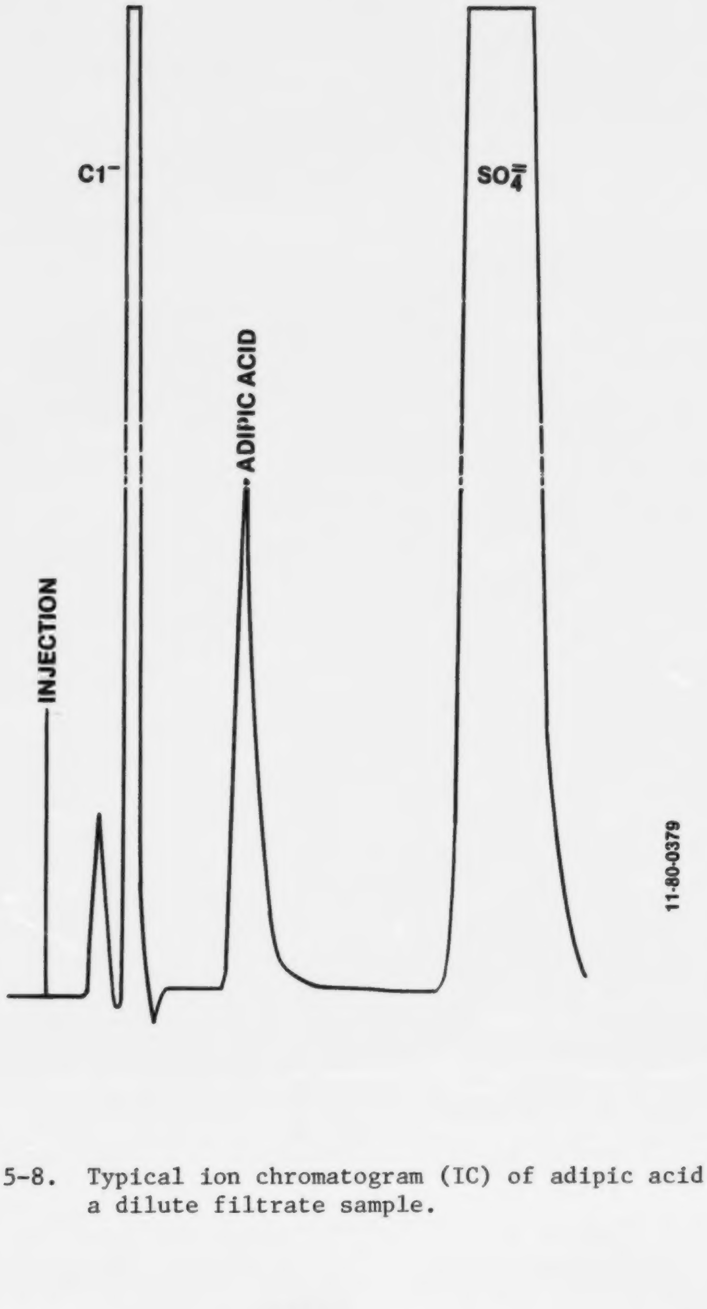

Figure 5-8. Typical ion chromatogram (IC) of adipic acid in a dilute filtrate sample.

TABLE 5-5. TYPICAL RETENTION TIMES AND RESPONSE FACTORS FOR IC ANALYSES OF MONO- AND DICARBOXYLIC ACIDS

Compound	Retention Time (Relative to Adipic)	Response Factor (Relative to Adipic)	Comments
Formic Acid	0.34	17.8	These compounds are seen in nearly all of the bench-scale samples. They appear as a sharp peak just before chloride. However, since all the compounds have the same retention time, they cannot be individually identified.
Propionic Acid	0.34	1.34	
Butyric Acid	0.34	0.88	
Acetic Acid	0.34	2.65	
Valeric Acid	0.56	0.19	Valeric acid cannot be quantified if chloride is present. Response factor is also quite low.
Glutaric Acid	0.98	1.46	Glutaric acid coelutes with acipic acid.
Adipic Acid	1.00	1.00	
Succinic Acid	1.05	1.55	Generally appears as a shoulder on the downscale side of the adipic acid peak. Quantitative results are difficult.
Malonic Acid	1.32	2.64	Malonic acid can be measured by IC.
Oxalic acid	2.54	2.38	Probably would be covered by the sulfate peak.
Chloride	0.48	----	
Shawnee Mystery Peak	1.15	Unknown	Can interfere with adipic acid analysis if column resolution is poor.
Sulfate	2.15	----	

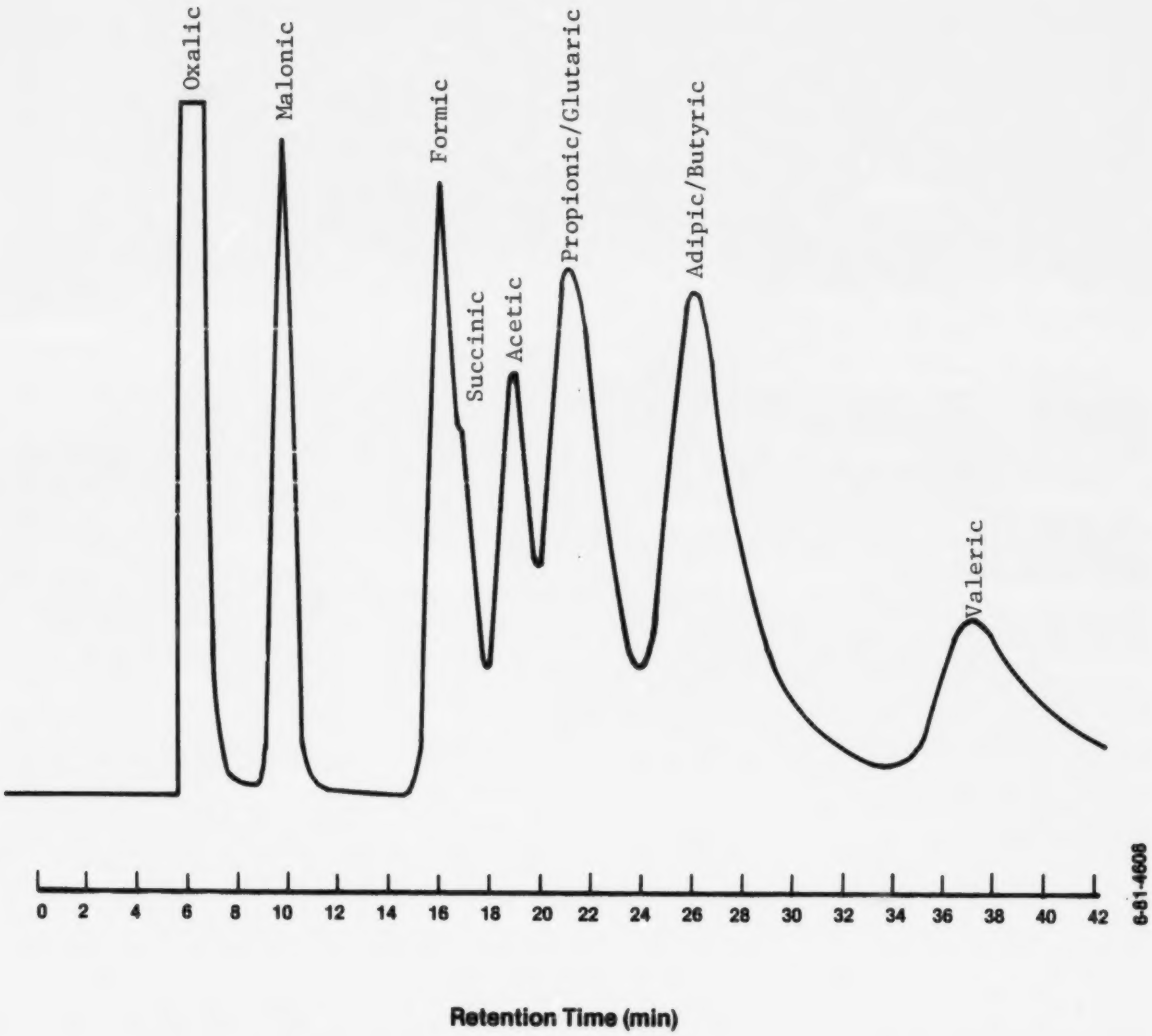

Figure 5-9. ICE chromatogram of an aqueous standard of ten carboxylic acids: 30.2 ppm oxalic, 20.2 ppm malonic, 12.2 ppm formic, 20.2 ppm succinic, 31.5 ppm acetic, 49.6 ppm propionic, 51.8 ppm glutaric,96.4 ppm butyric, 50.3 ppm adipic, 93.9 ppm valeric.

resolved at one time (Figures 5-10 and 5-11). Depending on their relative concentrations, three pairs of acids were unresolvable: formic and succinic; glutaric and propionic; adipic and butyric.

Table 5-6 provides typical elution and response results for the various mono- and dicarboxylic acids tested. Other compounds commonly observed in scrubber samples are also included in this table. The elution sequence can be partially predicted from the pK_a of the acid. The lower pK_a acids such as oxalic, malonic, formic, and succinic have the shortest retention times. As the acids become more aliphatic, however, Van der Waals forces become dominant and the elution order is less predictable. As a class, the dicarboxylic acids follow an orderly progression in retention times that corresponds to both pK_a and carbon chain length. The monobasic acids, on the other hand, have an elution order that appears to be dominated by chain length and does not follow pK_a. In general, the response is predictably lower for the acids with the longest retention times.

5.4 RESULTS OF DEGRADATION PRODUCT ANALYSES

Ion chromatography (IC) was used routinely throughout this study to determine the adipic acid concentration in scrubber filtrate samples. And, ion chromatography-exclusion (ICE) was used to measure the adipic acid concentration in scrubber solids samples. Due to certain time and equipment limitations, the quantitative capabilities of ICE and IC were not fully exploited with regard to the analysis of adipic acid degradation products. In general, ion chromatography techniques were only employed in a qualitative capacity to confirm the presence of adipic degradation products. Gas chromatography, however, was used extensively for the qualitative and quantitative determination of adipic acid degradation products. In most instances, the measurements made by IC or ICE were in reasonable agreement with those made by GC.

5.4.1 Analysis of Filtrates for Carboxylic Acids

Filtered slurry samples were collected at the end of twenty-three bench-scale runs and analyzed for nine different carboxylic acids by GC. Each

TABLE 5-6. TYPICAL RETENTION TIMES AND RESPONSE FACTORS FOR ICE ANALYSIS OF MONO- AND DICARBOXYLIC ACIDS

Compound	Structure	pK_1	Retention Time (Relative to Adipic)	Response Factor (Relative to Adipic)	Comments
Oxalic Acid	HO_2CCO_2H	1.27	0.31	5.8	These compounds are generally obscured by sulfate.
Malonic Acid	$HO_2CCH_2CO_2H$	2.3	0.43	2.2	
Formic Acid	HCO_2H	3.77	0.65	2.2	These compounds can be identified by ICE. Resolution of formic-succinic and glutaric-propionic may be difficult.
Succinic Acid	$HO_2C(CH_2)_2CO_2H$	4.21	0.68	1.4	
Acetic Acid	CH_3CO_2H	4.76	0.75	0.95	
Glutaric Acid	$HO_2C(CH_2)_3CO_2H$	4.30	0.82	1.2	
Propionic Acid	$CH_3CH_2CO_2H$	4.88	0.85	0.90	
Adipic Acid	$HO_2C(CH_2)_4CO_2H$	4.42	1.00	1.00	
Butyric Acid	$CH_3(CH_2)_2CO_2H$	4.86	1.01	0.65	Coelutes with adipic acid
Valeric Acid	$CH_3(CH_2)_3CO_2H$	4.78	1.41	0.37	Low response factor makes quantification of valeric acid difficult.
Shawnee Mystery Peak	---	----	0.58	unknown	Easily identified as this compound does not coelute with any of the other acids.
Sulfate	---	----	0.3+	----	

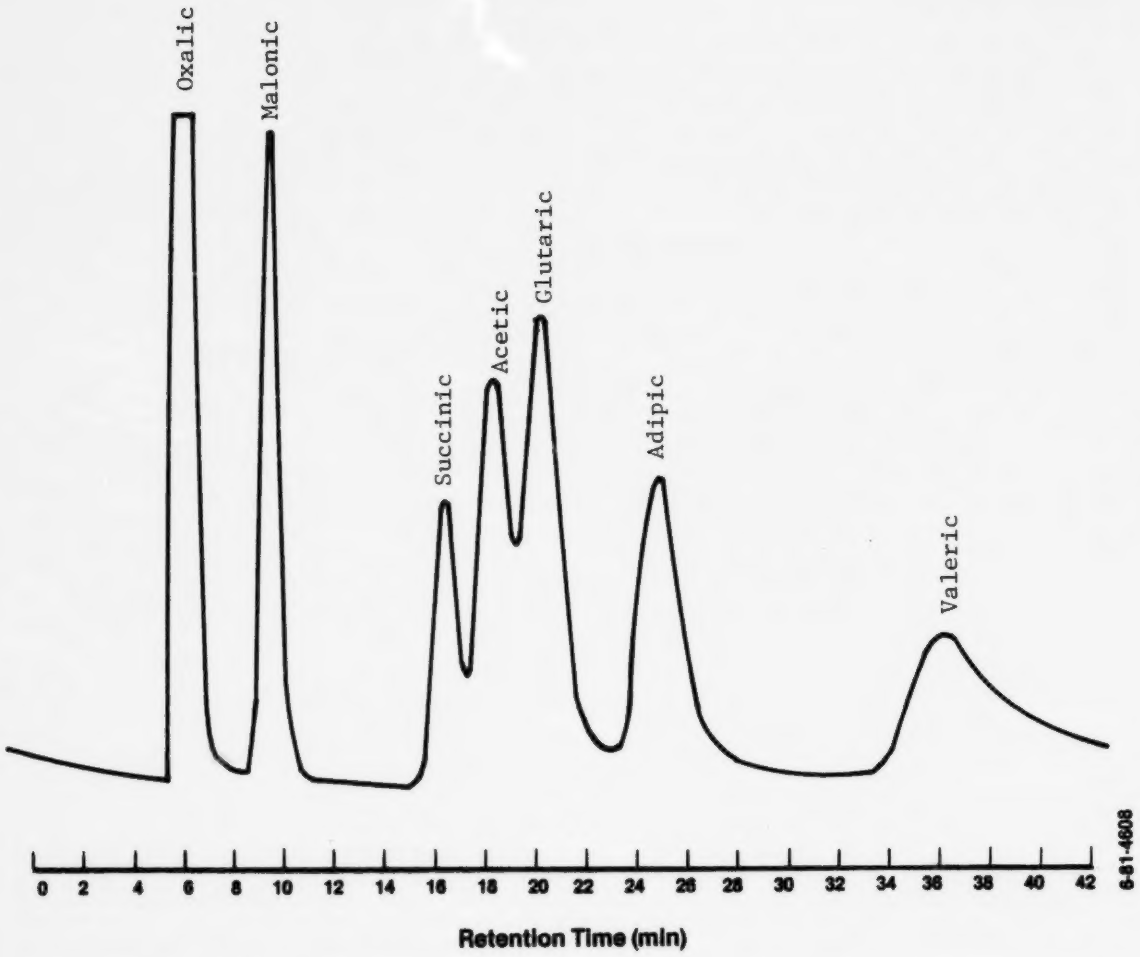

Figure 5-10. ICE chromatogram of an aqueous standard containing seven carboxylic acids: 30.2 ppm oxalic, 20.2 ppm malonic, 20.2 ppm succinic, 31.5 ppm acetic, 51.8 ppm glutaric, 50.3 ppm adipic, and 93.9 ppm valeric.

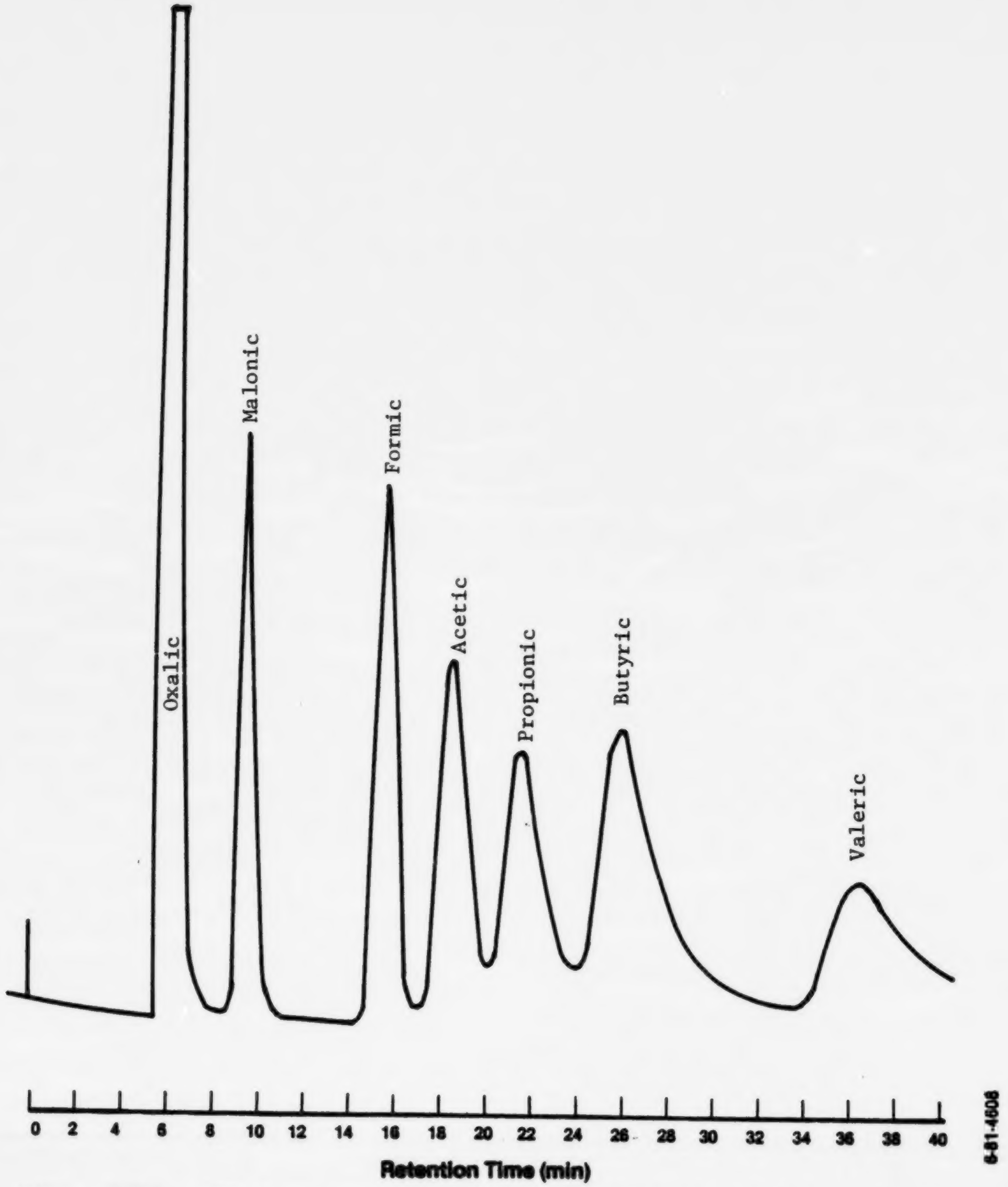

Figure 5-11. ICE chromatogram of an aqueous standard containing seven carboxylic acids: 30.2 ppm oxalic, 20.2 ppm malonic, 12.2 ppm formic, 31.5 ppm acetic, 49.6 ppm propionic, 96.4 ppm butyric, and 93.9 ppm valeric.

Each sample required a total of four separate determinations:

1) The aqueous sample was adjusted to pH 1 with concentrated HCl and injected directly into the GC. This provided qualitative and quantitative information regarding the monobasic carboxylic acid content of the sample.

2) The aqueous sample was adjusted to pH 1 with HCl, spiked with known amounts of acetic, propionic, butyric, and valeric acids, and injected into the GC. This provided confirmation of the results from Step 1.

3) The aqueous sample was extracted with diethyl ether, methylated with diazomethane, and the methylated ether extract was injected into the GC. This provided qualitative and quantitative information regarding the dibasic carboxylic acid content of the sample.

4) The methylated extract was spiked with known amounts of oxalic, malonic, succinic, glutaric, and adipic acid and injected into the GC. This provided confirmation of the results from Step 3.

Table 5-7 provides a summary of the GC results for scrubber filtrates from bench-scale runs #9-28, 30, 31, and 33. Based on detection limits, extraction efficiencies, and dilution factors, maximum undetectable concentrations have been calculated for the acids that were not detected and they are preceded by a less-than (<) sign. These values vary slightly from run to run due to differences in the dilution factors for the dilute filtrate samples that were analyzed.

The results contained in Table 5-7 lead to several conclusions:

- Valeric acid was identified in all but three samples, thereby lending support to conjugated oxidative decarboxylation as the degradation mechanism:

$$\underset{\text{adipic acid}}{HO_2C(CH_2)_4CO_2H} \xrightarrow[\text{attack}]{\text{free radical}} \underset{\text{valeric acid}}{CH_3(CH_2)_3CO_2H} + CO_2$$

  It is also of interest to note that in virtually every case, butyric and propionic acids were only detected if valeric

TABLE 5-7. RESULTS OF GC ANALYSES FOR FINAL BENCH-SCALE FILTRATE SAMPLE ADIPIC ACID DEGRADATION PRODUCTS

	Acid Concentrations[1], ppm									
Run #	Acetic[2]	Propionic[2]	Butyric[2]	Valeric[2]	Oxalic[3]	Malonic[3]	Succinic[3]	Glutaric[3]	Adipic[3]	Bench-Scale Scrubber Operating Conditions
R-9	<4	<3	<2	7	<63	<33	43	<28	2880	pH 4.6, natural oxidation, 22 hours
R-10	<3	<2	<2	23	<24	<13	27	<11	3430	pH 5.1, natural oxidation, 22 hours
R-11	<4	<3	<2	54	<32	<17	32	<14	2630	pH 5.5, natural oxidation, 12 hours
R-12	<3	15	<2	138	<29	80	38	23	2760	pH 5.1, forced oxidation, 18.5 hours
R-13	<4	17	<2	95	<30	66	37	73	2310	pH 4.6, forced oxidation, 18 hours
R-14	<3	<3	<2	52	<29	29	64	400	5310	pH 5.1, forced oxidation, 21 ppm Mn, 20 hours
R-15	<4	72	243	154	<16	<8	<10	<7	3280	pH 4.6, partial forced oxidation, 21.5 hours
R-16	<3	4	4	65	<15	<8	<9	<6	1700	pH 5.1, natural oxidation, 2 ppm Mn, 22 hours
R-17	<4	55	17	188	<16	22	<10	<7	3280	pH 4.6, forced oxidation, low temperature, 19 hours
R-18	<4	4	7	56	16	<9	265	622	2650	pH 5.1, forced oxidation, 5 ppm Mn, 22 hours
R-19	<4	238	<2	440	<16	238	62	74	1840	pH 5.1, forced oxidation, 20 hours
R-20	<4	<3	<2	330	<16	<9	<10	<7	5250	pH 5.5, natural oxidation, 22 hours
R-21	<4	<3	<2	124	<16	<8	<10	<7	2870	pH 5.5, natural oxidation, high sulfite, 22 hours
R-22	<4	<3	<2	290	<15	<8	<10	<7	3970	pH 5.1, natural oxidation, 20 hours
R-23	<3	<3	7	<2	<15	<8	<9	<6	1700	pH 5.1, natural oxidation, low adipic conc., 22 hours
R-24	<4	<3	<2	211	<14	<7	<9	<6	11580	pH 5.1, natural oxidation, high adipic conc., 18 hours
R-25	102	<3	<2	215	<15	109	65	234	2480	pH 4.6, forced oxidation, high temperature, 22 hours
R-26	69	157	195	262	<15	48	<10	55	1310	pH 4.6, forced oxidation, 22 hours
R-27	92	<3	<2	<2	<16	<8	<10	86	3000	pH 4.6, forced oxidation, 15 ppm Mn^{+2}, 20 hours
R-28	<4	<3	<3	<2	<18	<9	<11	<8	2940	pH 5.1, forced oxidation, thiosulfate, 19 hours
R-30	<4	29	13	27	<15	68	160	561	3080	pH 5.1, forced oxidation, Springfield limestone plus fly ash, 20 hours
R-31	<4	<3	10	20	<16	76	156	468	1550	pH 5.1, forced oxidation, 6 ppm Mn^{+2}, 2 ppm Fe^{+3}, 24 hours
R-33	<3	<2	<2	4	<14	<7	32	108	1960	pH 4.1, forced oxidation, 18 ppm Mn^{+2}, 23 hours

[1] Acid concentrations have been calculated for the undiluted filtrate.

[2] Monobasic acids: Average relative standard deviation = ±4% for 3 or more determinations.

[3] Dibasic acids: Uncertainty due to dilution and variable extraction efficiencies = 10-20%.

was also present. This lends credence to the stepwise oxidation process which is theorized to occur once valeric acid is formed (10).

- Large amounts of glutaric and succinic acid were formed in runs where manganese ions were present in the hold tank. Of the total amount of adipic acid degraded, from 13 to 41 percent could be accounted for as glutaric acid and up to 15 percent could be accounted for as succinic acid. In all other bench-scale runs, a maximum of 5 percent of the degraded adipic acid could be accounted for as glutaric acid. Apparently, the presence of manganese dramatically affects the degradation process by process by promoting the oxidative route and inhibiting the decarboxylative route. This, coupled with the preceding conclusion regarding the stepwise production of monocarboxylics, implies that adipic acid degrades by either a conjugated oxidative mechanism (i.e., adipic → glutaric → succinic → . . .) or a conjugated oxidative decarboxylation mechanism (i.e., adipic → valeric → butyric → . . .), and that there is little or no crossover between mechanisms once the process has begun. This is illustrated in Figure 5-12 by redrawing Figure 5-1 and omitting the arrows between dicarboxylic and monocarboxylic chains.

- Oxalic acid was not detected in any of the samples, therefore, it either was not generated or it decomposed too rapidly to be seen. Since virtually every other carboxylic acid was detected, it appears that oxalic was produced but was unstable. Oxalic is known to readily decompose to CO_2.

- Acetic acid was only detected in three of the twenty-three samples, which tends to imply either an analytical error or an anomalous degradation mechanism. Since no attempt was made to confirm the presence of acetic acid by an independent method, it is difficult to assess the significance of this GC result.

- The analyses of liquid phase degradation products showed that from 14 to 75 percent of the degraded adipic acid could be accounted for in the liquid phase. This assumes that each molecule of adipic acid produced only one degradation product molecule. In general, a higher percentage of the degraded adipic acid was recovered as degradation produces in the forced oxidation tests than the natural oxidation tests (43% versus 29%).

5.4.2 Analysis of Scrubber Gases for Hydrocarbons

Several samples of gas were taken from the head space above the slurry in the bench-scale scrubber. These were intended primarily to test the GC method for low molecular weight hydrocarbons, therefore, there was no attempt made to acquire samples from more than a couple of runs. It turned out that they also served to help substantiate the portion of the degradation scheme which predicts the production of n-paraffins (Figure 5-12).

Table 5-8 lists the results obtained with grab samples taken during the course of selected bench-scale test runs. Ethane, propane, and n-butane were observed in all samples. The data for run R-24B are perhaps the most interesting, since the samples analyzed represent both the initial and final conditions of the run. Assuming that the degradation of adipic acid is responsible for the concentrations of ethane (1.54 ppmv), propane (4.04 ppmv), and butane (1.70 ppmv) during R-24B, the amount of adipic acid degradation needed to account for these hydrocarbons, assuming each molecule of adipic acid yields only one hydrocarbon degradation product, is:

Adipic Acid Degradation Rate - 0.0425 g/hr

The observed degradation rate for run R-24 was 0.074 g adipic/hr. It appears that the gas phase degradation products can account for a significant fraction of the total adipic acid degraded, 57% in this case.

5.4.3 Analysis of Shawnee Samples

Prior to this bench-scale program, there were two routine methods for determining adipic acid in scrubber slurries: ion chromatography (IC) and the silicic acid separation method. In the course of this study, gas chromatography (GC) and ion chromatography-exclusion (ICE) methods were developed that are capable of quantitating adipic acid as well as its degradation products. A titrimetric method was also developed that addresses the overall buffer capacity over the pH range of 3-6 of mixtures containing adipic acid and other adipic species.

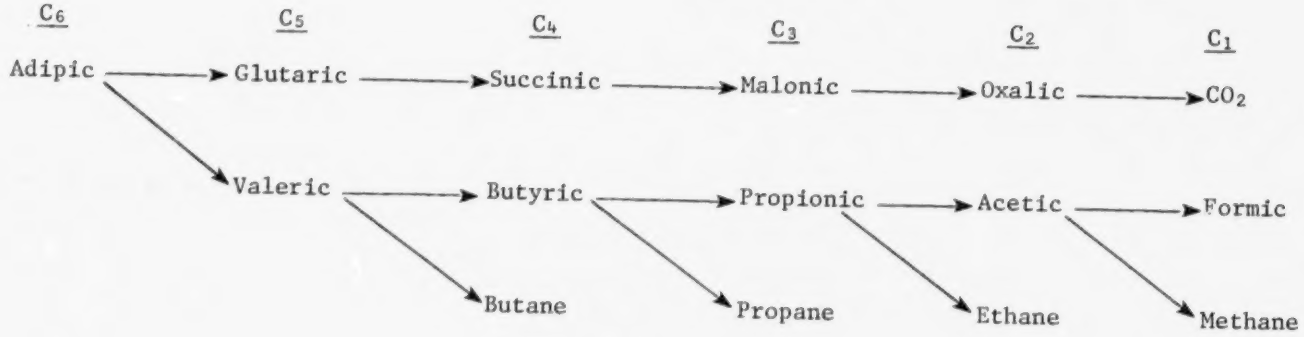
C_6
C_5
C_4
C_3
C_2
C_1
Adipic
Glutaric
Succinic
Malonic
Oxalic
CO_2
Valeric
Butyric
Propionic
Acetic
Formic
Butane
Propane
Ethane
Methane

Figure 5-12. Modified oxidative decarboxylation mechanism for adipic acid.

TABLE 5-8. SUMMARY OF HYDROCARBON ANALYSES ON GAS GRAB SAMPLES FROM SELECTED BENCH-SCALE SCRUBBER RUNS WITH ADIPIC ACID[1]

Run #	Time Sample Taken (hr)[2]	Methane (ppmv)	Ethane[3] (ppmv)	Propane[3] (ppmv)	Butane[3] (ppmv)	Conditions
R-24A	2	<1	1.96 ±.03	5.36 ±.11	1.87 ±.04	pH 5.1; natural oxidation; high adipic run; aborted after 3 hours
R-24B	2	<1	1.18 ±.01	3.03 ±.07	1.25 ±.06	Rerun; same conditions as above
	2.5	<1	1.44 ±.01	3.78 ±.11	1.44 ±.13	
	19	<1	1.54 ±.04	4.04 ±.09	1.70 ±.06	
R-25	22	<1	2.63 ±.02	2.91 ±.01	0.49 ±.11	pH 4.6; forced oxidation; high temperature

[1] No hydrocarbons were present in the synthetic flue gas.

[2] Time represents the total duration of the run at the time the grab sample was taken.

[3] Uncertainties represent the standard deviation for two or more analyses of the sample.

A practical demonstration of these techniques was provided by applying them to a filtered slurry sample obtained from the Shawnee test facility. The sample was taken on 3/27/81, near the end of a three month reliability test. Table 5-9 summarizes the results of the analyses performed on this sample.

TABLE 5-9. RESULTS OF ANALYSES OF SHAWNEE FILTRATE[1]

Type of Analysis	[Adipic], ppm	Degradation Products Identified, ppm
silicic acid (by Shawnee)	1173	not applicable
silicic acid (by Radian)	1200	not applicable
buffer titration (by Radian)	790	not applicable
ICE (by Radian)	512	glutaric, 26; succinic, 22 Shawnee mystery compound, 456 (as adipic)
GC (by Radian)	540	succinic, 15; butyric, 5; acetic, 15
IC (by Radian)	652	Shawnee mystery compound, 2015 (as adipic)

[1] Shawnee scrubber feed sample from two-tank forced oxidation reliability test. Sample taken on 3/27/81.

In order to put the above results in perspective, we must look at the relative specificities of each of these analytical methods. The GC and ICE results are both highly specific to adipic acid. These results show that the actual concentration of adipic acid is around 530 ppm. The IC result of 652 ppm reflects the fact that glutaric acid, and perhaps succinic acid, can coelute with adipic acid. And, both glutaric and succinic acids have response factors higher than adipic acid on IC. The buffer titration result of 790 ppm reflects the presence of all acids, including adipic acid and its mono- and dicarboxylic degradation products, which have pK_a values between 3 and 6. The high results seen for the silicic acid technique cannot be accounted for by the concentration of the standard mono- and dicarboxylic acids found in the sample. Further investigation of the silicic acid technique revealed that the error in this analysis is related to the presence of apparently high concentrations of the so-called Shawnee mystery compound. The results of this investigation are reported in Section 6-2.

SECTION 6

RESULTS OF ADDITIONAL LABORATORY TESTING

The results of additional laboratory investigations are presented in this section. In Section 6-1, the results of an investigation involving sample stability is presented. This work was performed as a result of continuing decomposition of adipic acid in some of the samples obtained during bench-scale testing at Springfield.

A limited investigation of the so-called Shawnee mystery compound has been performed. Although this work was not a part of the original scope of work, these analyses were performed to gain more insight into the adipic acid degradation phenomena. The results of this investigation are presented in Section 6-2.

An effect of adipic acid on solid phase crystal structure and size has been reported (9). Several scanning electron micrographs (SEM) have been taken of solids obtained from a variety of sources. The results of this investigation are presented in Section 6-3.

6.1 SPRINGFIELD SAMPLE DECOMPOSITION TESTING

In addition to the four runs (P-1 through P-4) reported in Section 3.3.3 for bench-scale scrubber testing at Springfield, several more test runs were made. However, the results of these tests were not interpretable due to unexpected and continuing chemical degradation of adipic acid in the sample solutions. The samples from tests P-1 through P-4 were analyzed on-site at Springfield within hours of sample collection. The remainder of the samples were analyzed after shipment back to Radian's Austin laboratories, about one week after sample collection. The chemical degradation results calculated

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for the later Springfield runs were much higher than anticipated and upon subsequent reanalysis of the samples, continuing adipic acid degradation was observed. Reanalysis of samples from the Shawnee tests and the previous laboratory bench-scale tests showed that significant continuing decomposition seemed to be unique to the Springfield samples. A series of synthetic scrubber solutions were prepared containing various materials suspected to be causing the problem. The parameters tested include H_2O_2 (used to fix sulfite in solution), Mn^{+2}, SO_3^{-2}, Fe^{+3} and Springfield limestone. The test matrix is given in Table 6-1.

The first eight samples represent a factorial test design between H_2O_2, $SO_3^{=}$, and Mn^{+2}. Tests 9 and 10 were designed to test the effect of the Springfield limestone, with and without H_2O_2. Test 11 was designed to determine if Fe^{+3} caused decomposition and Test 12 was designed to evaluate the effect of the adipic acid concentration on the decomposition rate.

The pH of all samples was adjusted to 5.0. Samples 9 and 10, which contained the Springfield limestone, were prepared by adding small amounts of limestone and then adjusting the pH back to 5.0 with sulfuric acid. A total of 12.5 g of limestone was added to each 500 mL sample. An analysis of the Springfield limestone is given in Table 6-2. Each sample was analyzed immediately after it was prepared and two additional times after standing for one and two weeks, respectively. The results of these analyses are given in Table 6-3.

The results show significant decomposition (decrease in adipic acid concentration) in Tests 2, 4, 10, 11 and 12. Other than this, no statistically significant trends can be identified within the precision of the measurements, ±2 percent. There is, however, another indication of decomposition. In some of the tests, a distinct new peak was observed during ion chromatographic (IC) analysis of the samples. This peak was in the same location as those seen during the analysis of the decomposing samples from Springfield and also corresponds to the unidentifiable IC peak usually seen in adipic acid scrubber solutions from the Shawnee test facility. Analysis of the IC chromatograms indicate the following:

TABLE 6-1. LABORATORY DECOMPOSITION TESTING SAMPLE MATRIX

Sample No.	Adipic Acid Concentration, ppm	H_2O_2 1600 ppm	Mn^{+2} 8 ppm	$SO_3^=$ ≈400 ppm	Fe^{+3} <9 ppm	Springfield Limestone	$SO_4^=$ ≈400 ppm
1	3000	X					X
2	3000	X	X				X
3	3000	X		X			X
4	3000	X	X	X			X
5	3000						X
6	3000		X				X
7	3000			X			X
8	3000		X	X			X
9	3000			X		X	>>400 ppm
10	3000	X		X		X	>>400 ppm
11	3000	X		X	X		X
12	1000	X	X	X			X

TABLE 6-2. ICAPES[1] SCREENING ANALYSIS OF SPRINGFIELD LIMESTONE

Element	Concentration, ppm	Element	Concentration, ppm
Al	57	Mo	<1.0
Ba	420	Na	200
Co	<3.0	Ni	<1.5
Cu	<0.5	P	<90
Cr	<0.5	Si	41
Fe	160	Sr	<0.1
K	110	Ti	<0.5
Li	<0.1	V	<1.5
Mg	1400	Y	20
Mn	430	Zn	15

[1] Inductively coupled argon plasma emissions spectroscopy

TABLE 6-3. ANALYTICAL RESULTS OF LABORATORY DECOMPOSITION TESTS

	Adipic Acid Concentration, ppm				Decomposition Rate, ppm/day	
Run	First Analysis	(Date)	Second Analysis 10/14/80	Third Analysis 10/21/80	First to Second Analysis, ±20 ppm/day	First to third Analysis, ±9 ppm/day
1	2997	(10/7)	2952	2810	6.4	13
2	3000	(10/7)	2788	2500	30	36
3	2995	(10/7)	2970	2902	3.6	6.6
4	3017	(10/7)	2807	2564	30	32
5	2991	(10/8)	2984	2862	1.2	9.9
6	3003	(10/8)	3046	3009	-7.2	-0.5
7	2982	(10/8)	2984	2898	-0.3	6.5
8	3003	(10/8)	3083	2917	-13	6.6
9	3023	(10/8)	3064	2802	-6.8	17
10	3005	(10/8)	2419	2381	98	48
11	3010	(10/8)	2879	2842	22	13
12	998	(10/8)	848	761	25	18

- Samples with no peroxide (5, 6, 7, 8 and 9) showed no significant decrease in adipic acid concentration and there was no peak or shoulder near the adipic acid IC peak.

- Samples with peroxide only (1 and 3) showed a small shoulder indicating a very low rate of decomposition and no significant decrease in adipic acid concentration.

- Samples with both peroxide and Mn^{+2} (2, 4 and 12) showed a significant second IC peak. Neither peroxide nor Mn^{+2} alone caused significant adipic acid decomposition, but together, rapid decomposition was observed. It may also be significant that adipic acid decomposition occurred in test 2 in the absence of sulfite oxidation.

- The sample with peroxide and Fe^{+3} (11) also showed a significant second IC peak although it was not quite as large as those observed in Tests 2, 4, and 12.

- The sample with peroxide and Springfield limestone (10) showed the largest second peak of any of the samples and a large decrease in adipic acid concentration.

An attempt was made to identify the material causing the new IC peak by running a series of mono- and dicarboxylic acids as spikes in the test samples using IC, ion chromatography-exclusion (ICE) and gas chromatography-mass spectroscopy (GC-MS). However, of the materials tested (glutaric acid, succinic acid, malonic acid, valeric acid, butyric acid, propionic acid, acetic acid and formic acid) no positive identification could be made.

The results of these tests have significance beyond simply understanding why the test samples from Springfield decomposed. The catalytic effects of Mn^{+2} and the trace elements from the Springfield limestone are most likely related to the effect of these materials in decreasing the adipic acid degradation rate in scrubber systems. It was also notable that a new IC peak appeared in proportion to the degradation of adipic acid and that this peak is most likely composed of the so-called Shawnee mystery compound.

6.2 RESULTS RELATING TO THE SHAWNEE MYSTERY PEAK

One of the phenomena relating to the use of adipic acid in FGD systems is the formation of an unknown degradation product. This compound was first observed at TVA's Shawnee test facility and was dubbed the Shawnee Mystery Peak because it interfered with their analysis of adipic acid by IC chromatography.

Although the identification of the Shawnee mystery compound was not part of the scope of work on this project, several observations have been made during the course of bench-scale testing. These observations are reported here for the aid of future investigators. Results relating to the Shawnee mystery compound are listed below:

1) The mystery compound has been located on chromatograms from both IC and ICE analyses.

2) The mystery compound is not extracted from scrubber solutions at low pH with ether as are the "standard" mono- and dicarboxylic acid degradation products.

3) The mystery compound can be synthesized by boiling solutions containing only adipic acid, peroxide, and low levels of $MnSO_4 \cdot H_2O$.

4) The mystery compound is analyzed as a carboxylic acid by the silicic acid technique.

The first two of these results are illustrated in Figure 6-1 which shows four chromatograms of the same Shawnee filtrate sample. The sample was obtained after a three-month reliability test using two-tank forced oxidation at pH 5.1. Figure 6-1a and 6-1b show an IC and ICE chromatogram of the original sample. The position of the mystery peak in Figure 6-1b was found not to correspond with any of the "standard" mono- or dicarboxylic acid degradation products.

Figures 6-1c and 6-1d show the same sample after low pH-ether extraction of the carboxylic acids. In each case the mystery peak has remained in the

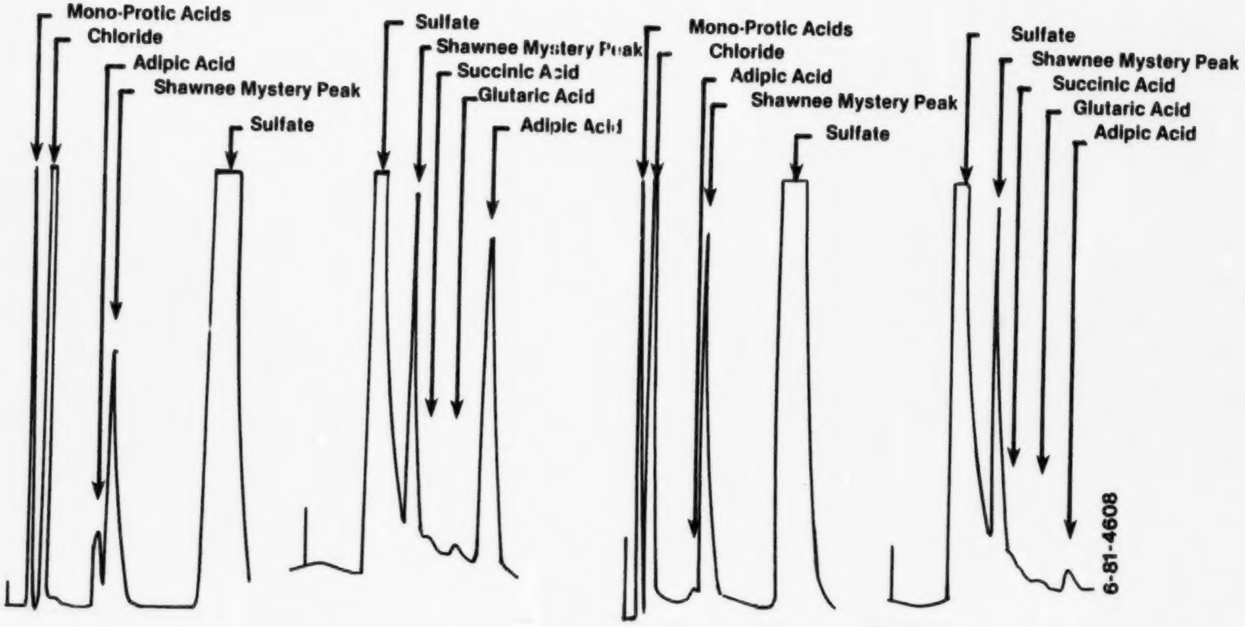

Figure 6-1a
IC Analysis of Shawnee
Scrubber Filtrate

Figure 6-1b
ICE Analysis of
Shawnee Scrubber
Filtrate

Figure 6-1c
IC Analysis of Shawnee
Scrubber Filtrate After
Ether Extraction.

Figure 6-1d
ICE Analysis of
Shawnee Scrubber
Filtrate After Ether
Extraction.

Figure 6-1. IC and ICE chromatogram of Shawnee filtrate before and after ether extraction.

aqueous phase while the acids have been extracted by the ether. This would seem to suggest that the mystery compound remains ionized (or unprotonated) at low pH. It also explains why we have been unable to locate the mystery compound by GC since the GC procedure involves low pH ether extraction followed by methylation of the extracted acids.

Small quantities of what appears to be the mystery compound have been synthesized by simply boiling an adipic acid solution in the presence of H_2O_2 and 20 ppm Mn^{+2} (as $MnSO_4 \cdot H_2O$). However, this procedure also results in the production of large quantities of the other "standard" degradation products (predominantly the dicarboxylics). And, eight sequential ether extractions of this mixture failed to produce a pure solution containing only the mystery compound.

The Shawnee sample shown in Figure 6-1 would appear to contain significant quantities of the mystery compound. This particular sample has been analyzed by a number of analytical methods. The results are shown in Table 6-4.

In order to put the results in Table 6-4 into perspective, we must look at the relative specificities of these five analytical methods. The ICE and GC methods are quite specific for adipic acid. The results of these analyses show that the actual concentration of adipic acid is slightly above 500 ppm. Note that the GC method does not detect the Shawnee mystery compound. As described above, this is because the mystery compound is not extracted into ether at low pH.

The IC determination shows an apparent concentration of about 650 ppm adipic acid. However, in the IC analysis, glutaric acid and possibly succinic acid coelute with adipic acid and their response factors are also somewhat higher than adipic acid (see Table 5-5). With this combination of factors in mind, the IC result for adipic acid is about what would be expected.

TABLE 6-4. RESULTS OF COMPARATIVE ANALYSES FOR A SHAWNEE FILTRATE SAMPLE[1]

Type of Analysis	Adipic Acid Concentration, ppm	Degradation Products Identified, ppm
ICE (by Radian)	512	Shawnee Mystery Peak, 456 ppm (as adipic acid); glutaric acid, 26 ppm; succinic acid, 22 ppm.
GC (by Radian)	540	Shawnee Mystery Peak, not detected; succinic acid, 15; butyric acid, 5; acetic acid, 15.
IC (by Radian)	652	Shawnee Mystery Peak, 2015 ppm (as adipic acid)
Buffer titration (by Radian)	790	Not applicable
Silicic acid (by Radian)	1200	Not applicable
Silicic acid (by Shawnee)	1173	Not applicable

[1] Sample taken from scrubber feed on 3/27/81.

The buffer titration method involves a titration over the pH range of 3 to 6. Therefore, it is relatively insensitive to stronger acids with a pK_a less than 3. The adipic acid degradation products identified by GC and ICE have pK_a values between 3 and 6 and *analyze as adipic acid by this technique*. This accounts for most of the deference between the *apparent* adipic acid concentration of 790 ppm determined by the buffer titration method and the *actual* adipic acid concentration as determined by ICE and GC.

The high silicic acid results for this sample (≈ 1200 ppm adipic acid) cannot be explained in terms of the standard mono- and dicarboxylic degradation products as the silicic acid results are greater than twice that determined by ICE and GC. It would seem quite likely that this discrepancy is the result of the mystery compound which, according to the IC and ICE analyses, is present in substantial concentrations.

Important steps in the silicic acid technique include:

- acidification of the sample with H_2SO_4 to protonate the carboxylic acids;
- absorption of the sample onto solid silicic acid;
- eluting of the organic acids off the silicic acid with a chloroform-butanol mixture (water, sulfate, chloride, and other inorganics remain trapped in the silicic acid); and
- titration of the chloroform-butanol mixture to pH 7 with a standard NaOH solution.

The net effect of the silicic acid procedure is a measurement of the total carboxylic acid content of the sample. An investigation of this technique showed that the mystery compound was present in the final chloroform-butanol extract. In this experiment, the silicic acid technique was performed using the Shawnee filtrate. Rather than titrating the final chloroform-butanol extract, this mixture was evaporated by vacuum distillation and the resulting solids were redissolved in water. IC analysis of this solution showed that the mystery compound was present along with the adipic acid and the other carboxylic acid degradation products. These results imply that the mystery compound is an acidic species since there is no other way to account for the high apparent adipic acid concentration as determined by the silicic acid technique. Since the presence of the mystery compound is not detected by the buffer titration technique, which measures buffer capacity over the pH range of 3 to 6, it would also appear that the mystery compound is a relatively strong acid with a pK_a value of less than 3.

Some limited efforts were made to isolate the mystery compound using a combination of the silicic acid technique and ether extraction. The methodology consists of low pH extractions of the Shawnee filtrate with ether to remove adipic acid and the mono- and dicarboxylic acid degradation products followed by removal of the inorganic matrix using silicic acid. Small quantities of pure mystery peak solutions have been prepared in this manner. However, initial attempts at producing larger quantities of the mystery compound suitable for analyses were not successful due to sulfuric acid breakthrough during the silicic acid portion of the procedure. Time limitations prevented further efforts in this area.

During the early portion of the three month adipic acid reliability testing at Shawnee, the adipic acid concentration (as determined by the silicic acid technique) was maintained at 1350 ppm. Roughly mid-way through the test program, an unexplained decrease in SO_2 removal was observed. Following this observation, a portion of the hold tank slurry was dumped and the level of adipic acid was increased to 1700 ppm (15). A sample of the Shawnee filtrate taken just prior to the increase in the adipic acid concentration was analyzed by Radian on ICE. The results show that the actual concentration of adipic acid was only 630 ppm instead of the 1350 ppm believed to be in the sample based on the silicic acid analyses. The concentration of the mystery compound was 696 ppm (as adipic acid on ICE). The relatively low concentration of adipic acid is probably the cause of the drop in SO_2 removal observed at Shawnee. Note that if the mystery compound is an acidic species with a pK_a value of less than 3, it would be of little use in enhancing SO_2 removal.

One additional clue regarding the nature of the Shawnee mystery compound can be offered. The formation of the mystery compound seems to be linked to the presence of manganese. In the sample decomposition tests reported in Section 6-1, the combination of peroxide and manganese resulted in the formation of the mystery compound. In results reported earlier in this section, the mystery compound was produced along with a variety of other carboxylic acids, by boiling solutions containing only peroxide, manganese, and adipic acid. The Shawnee filtrate also contains high concentrations of manganese.

In bench-scale runs performed under conditions similar to those at Shawnee, (i.e. manganese ions), large concentrations of glutaric acid were found (see Section 3.3.2). In the Shawnee sample, however, the concentration of glutaric acid was far below that which would be expected based on the bench-scale results. This suggests that the mystery compound may be directly involved, perhaps as an intermediate, in the formation or degradation of glutaric acid.

6.3 INVESTIGATION OF THE EFFECTS OF ADIPIC ACID ON CRYSTAL MORPHOLOGY AND SIZE

Waste solids generated in throwaway flue gas desulfurization systems are typically disposed of by ponding or by landfill of filtered solids. The economics of the disposal options due to differing equipment and land requirements are highly dependent on the quality and quantity of waste product. A significant decrease in the dewatering properties of a FGD sludge can dramatically reduce the lifetime of a disposal site. When additives are used, such as adipic acid, poor dewatering results in an increased loss of the additive in the liquids contained in the waste product.

An investigation of the dewaterability of FGD solids at the EPA/RTP pilot facilities has shown that lower filter efficiencies were observed when adipic acid was present (9). A possible explanation of this effect is a change in crystal size and/or morphology due to the presence of adipic acid. To investigate this effect, scanning electron micrography (SEM) of selected solid samples were obtained. The selected solids included:

- Solids generated during the batch precipitation tests (Section 4.1) in which the level of adipic acid was varied over a wide range,
- Solids generated during bench-scale testing. Solids from natural oxidation runs were selected based on the level of adipic acid in the liquid, and
- Solids obtained from the full-scale adipic acid demonstration program in Springfield, MO.

The operating conditions and additional solids information relating to this investigation are summarized in Table 6-5.

TABLE 6-5. PARAMETERS RELATED TO THE SOLIDS SELECTED FOR INVESTIGATIONS INTO PARTICLE SIZE AND PARTICLE MORPHOLOGY DIFFERENCES

Sample Identifiers	Slurry		Solids		Figure
	pH	$[H_2Ad]_\ell$ (ppm)	Oxidation (%)	$[H_2Ad]_s$ (ppm)	
Batch-tests					
Bτ-8B	4.6	6600	13	26600	6.2
Bτ-1B	4.6	0(a)	27	<500	6.3
Bench-scale					
R-23	5.1	876	13	1860	6.4
R-22	5.1	2890	28	5000	6.5
R-24	5.1	6780	43	7970	6.6
R-36	5.1	5620	99	<200	6.7
R-35(b)	4.6	2570	98	320	6.8
Springfield full scale					
212	5.5	0	98	0	6.9
623(c)	4.7	1750	98	N.A.	–

where: $[H_2Ad]_\ell$ = liquid phase adipic, $[H_2Ad]_s$ = solid phase adipic corrected for entrained filtrate.

Notes: (a) 3100 ppm adipic added after crystal formation, (b) manganese and iron additive test, (c) sample collected under conditions attributed to limestone blinding.

In a related investigation, the Radian equilibrium program was used to determine the relative saturation of scrubber species in some of the bench-scale runs. The runs selected for this investigation were natural oxidation runs in which the adipic acid concentration was varied from 876 to 7970 ppm. The SEM analyses from the bench-scale tests included the solids from these runs.

The solids from the full-scale FGD unit in Springfield were generated under forced oxidation conditions. The samples include solids precipitated with and without adipic acid in the system. In addition, a solid sample was obtained during a period of "limestone blinding". The limestone blinding phenomena was observed at Springfield when the flow of oxidation-air required for complete oxidation of the solids could not be maintained. Presumably, the sulfite ion concentration builds to the point where calcium sulfite precipitates on the surface of the limestone particles which prevents limestone dissolution. The net effect is a drop in pH which results in excess limestone consumption.

To test for surface precipitated calcium sulfite on the limestone particles, x-ray fluoresence, coupled with scanning electron microscopy, was used to analyze the Springfield solids. This technique allows the composition of individual crystals to be determined up to a depth of two microns.

The results of the investigations described above are summarized below:

- Natural oxidation solids from both the batch precipitation tests and the bench-scale tests showed a decrease in particle size with increasing liquid phase concentrations of adipic acid. However, in the forced oxidation solids from Springfield, no apparent effect of the adipic acid concentration on crystal size was observed.

- The crystal morphology of batch precipitation test solids appeared to change as a function of liquid phase adipic acid concentration for the high sulfite solids. The high sulfite solids formed in the presence of increasing liquid phase adipic acid showed a decrease in individual particle size, an increase in aggregate structure, and a dramatic increase in coprecipitated adipic acid.

- X-ray fluoresence spectroscopy of the Springfield blinding sample did not show excessive sulfur to be present on the surface of the particular limestone particle analyzed.

- The results from the Radian equilibrium program showed a slight increase in the calcium sulfite relative saturation. An increase in the calcium sulfite relative saturation increases the calcium sulfite nucleation rate which may explain the observed decrease in particle size.

The above results indicate that there are two factors which may impact the crystal size and morphology.

1) The liquid phase adipic acid concentration (which determines, in part, the amount of coprecipitated adipic acid in the solids), and

2) An increase in the calcium sulfite relative saturation (which may increase the nucleation rate and thereby decrease particle size).

Since these two factors occur in conjunction with each other, it is difficult to determine the relative importance of each of these effects.

Figure 6.2 and Figure 6.3 show solids formed during the early batch precipitation tests. The decrease in individual particle sizes and the increase in aggregate structure with increasing adipic acid coprecipitate is clearly indicated in these two illustrations. The solids of Figure 6.2 contain 26,6000 ppm adipic acid whereas the solids of Figure 6.3 contain less than 500 ppm adipic. The thin square individual particles best seen in Figure 6.3 are called platelets. These platelets are characteristic of solids generated under natural oxidation conditions. The extensive aggregate structure seen in Figure 6-2 is most likely the result of the extremely high adipic acid concentrations used in this batch precipitation test.

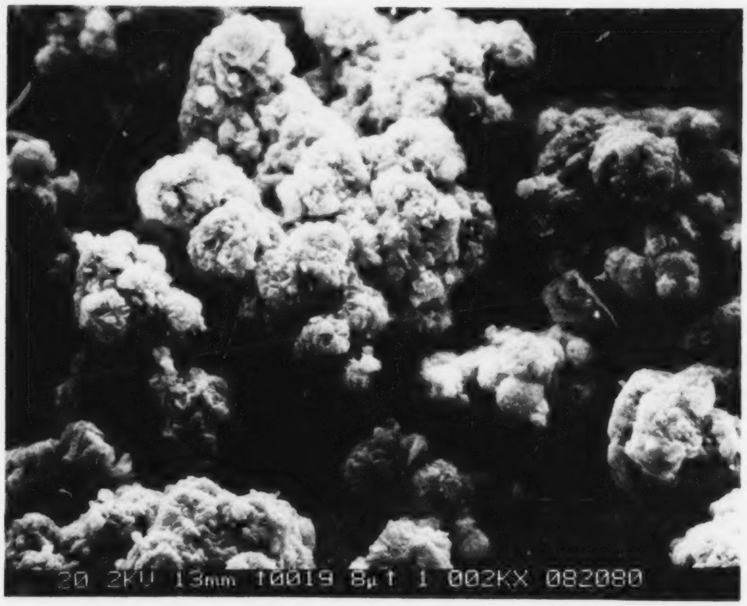
20 2KU 13mm 10019 8μ 1 002KX 082080

Figure 6-2. Batch test solids BT-8B (1000X).
Solids: 26,600 ppm coprecipitated adipic acid, 13% oxidation.
Slurry: 6,600 ppm liquid phase adipic acid.

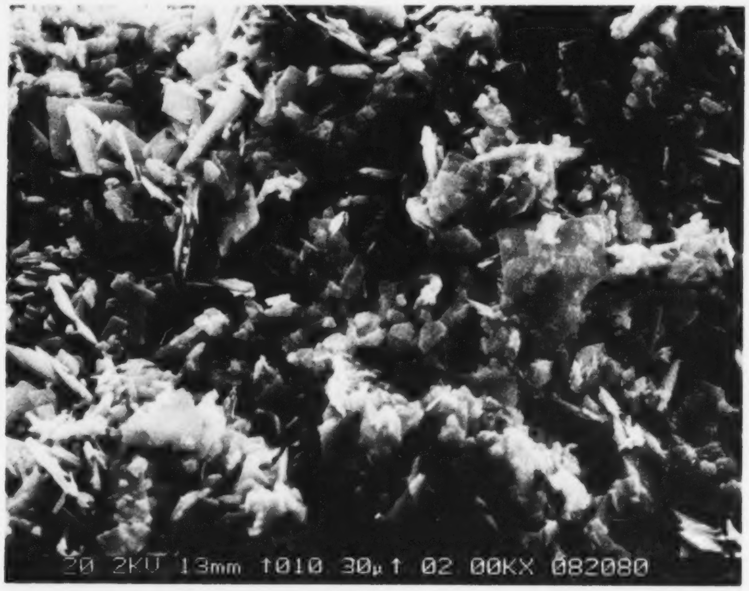
20 2KU 13mm 010 30μ 02 00KX 082080

Figure 6-3. Batch test solids BT-1B (2000X).
Solids: <500 ppm coprecipitated adipic acid, 27% oxidation.
Slurry: 3100 ppm liquid phase adipic acid added after precipitation.

The decrease in individual particle size with an increase in coprecipitated adipic acid was again demonstrated in the solids from the bench-scale tests. Solids from three of these tests are illustrated in Figures 6-4, 6-5, and 6-6. These solids were generated in the presence of increasing concentrations of adipic acid were found to contain increasing concentrations of coprecipitated adipic acid. As with the batch test results the individual platelet sizes decrease with increasing adipic acid concentrations. And, the aggregate structure seems to be approaching that seen in Figure 6-2 as the concentration of coprecipitated adipic acid increases. It is noteworthy that the solid phase oxidation increases with increasing adipic concentrations. This increase in oxidation could be expected to increase particle sizes; however, an effect opposite to that was observed.

Solids formed under forced oxidation conditions have been shown to contain very little coprecipitated adipic acid (Section 4.2). The decrease in particle size with increases in liquid phase adipic acid is not observed for these predominantly gypsum crystals. The solids pictured in Figure 6.7 and Figure 6.8 were generated during forced oxidation (100%) bench-scale runs. Both sets of crystals are of similar size despite differences in the liquid phase adipic acid concentration. These solids are generally larger than the naturally oxidized solids shown previously. And, no aggregate structures were visible in any of the SEM photographs taken of the forced oxidized solids. It is this lack of aggregate structure and larger size which allows the predominately gypsum solids to dewater more effectively than sulfite solids.

The SEM photograph in Figure 6-9 is of forced oxidized solids obtained from the full-scale demonstration unit at Springfield, MO. The particle size and morphology illustrated in Figure 6-9 is representative of the two force oxidized samples examined. No differences were observed between these solids, samples generated when adipic acid was present, or solids present in the system during limestone blinding conditions. As shown by comparing the SEM photographs in Figures 6-8 and 6-9, the solids from the full scale unit

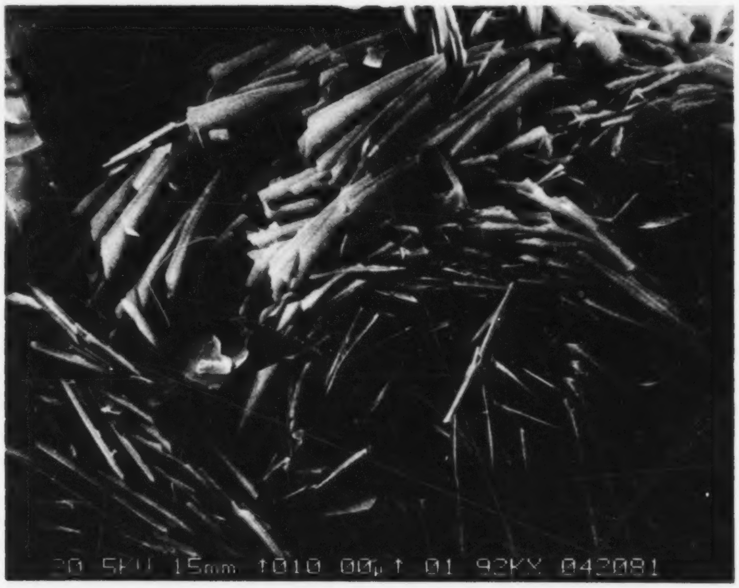
30 5KV 15mm 1010 00μ 01 92KX 042081

Figure 6-4. Bench-scale test solids R-23 (1920X).
Solids: 1860 ppm coprecipitated adipic acid.
Slurry: pH 5.1, 876 ppm liquid phase adipic acid.

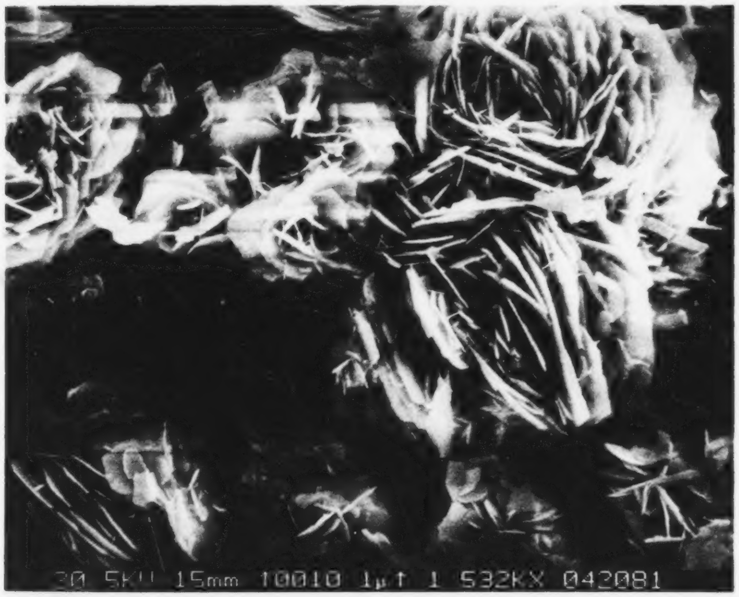
30 5KV 15mm 10010 1μ 1 532KX 042081

Figure 6-5. Bench-scale test solids R-22 (1532X).
Solids: 5000 ppm coprecipitated adipic acid, 28% oxidation.
Slurry: pH 5.1, 2890 ppm liquid phase adipic acid.

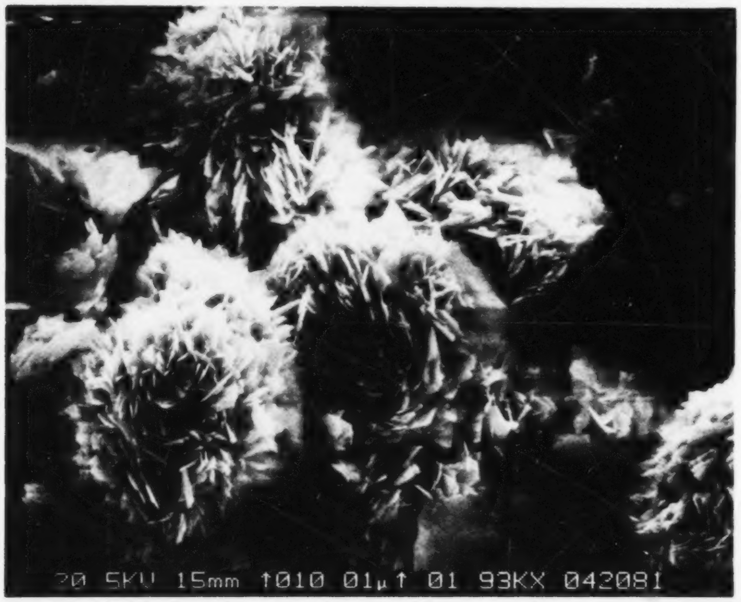
20 5KV 15mm ↑010 01μ↑ 01 93KX 042081

Figure 6-6. Bench-scale test solids R-24 (1930X).
Solids: 7970 ppm coprecipitated adipic acid.
Slurry: pH 5.1, 6780 ppm liquid phase adipic.

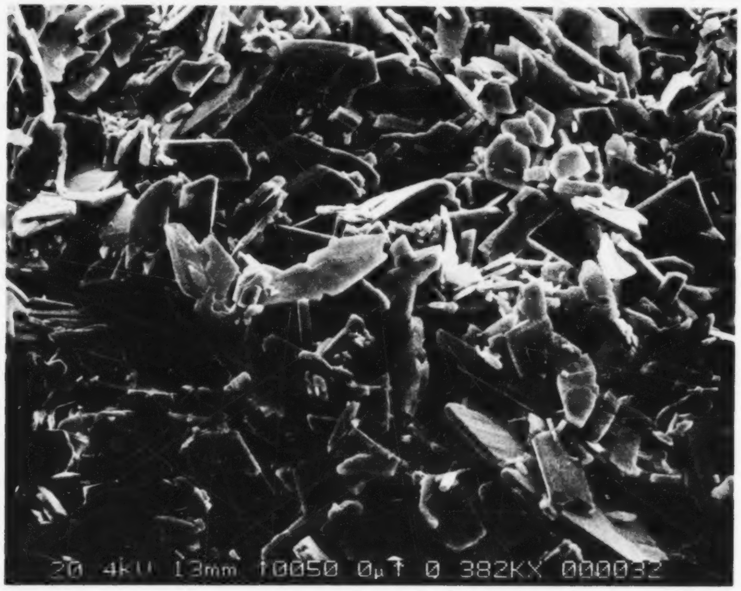
20 4KV 13mm ↑0050 0μ↑ 0 382KX 000032

Figure 6-7. Bench-scale test solids R-36 (382X)
Solids: <200 ppm coprecipitated adipic acid, 99% oxidation
Slurry: pH 5.1, 5620 ppm liquid phase adipic acid.

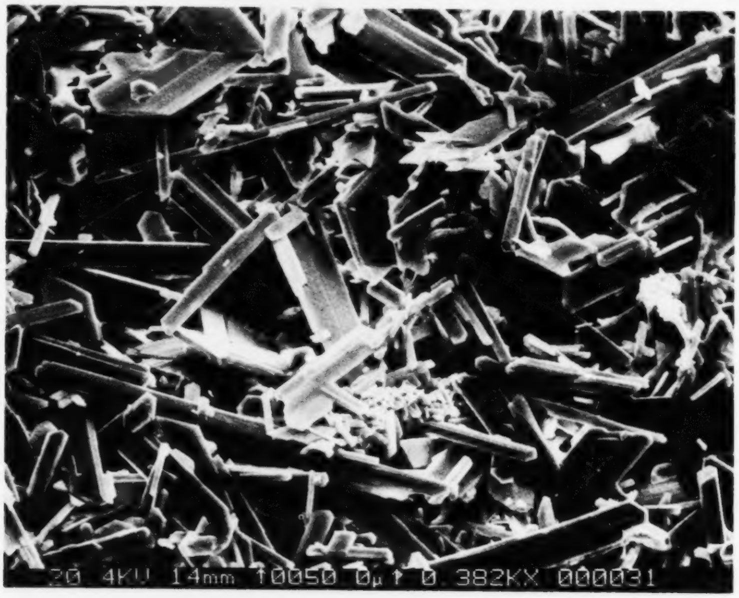
20 4KU 14mm ↑0050 0μ↑ 0 382KX 000031

Figure 6-8. Bench-scale test solids R-35 (382X).
Solids: 320 ppm coprecipitated adipic acid, 98% oxidation.
Slurry: pH 4.6, 2570 ppm liquid phase adipic acid (Mn^{+2} + Fe^{+3}).

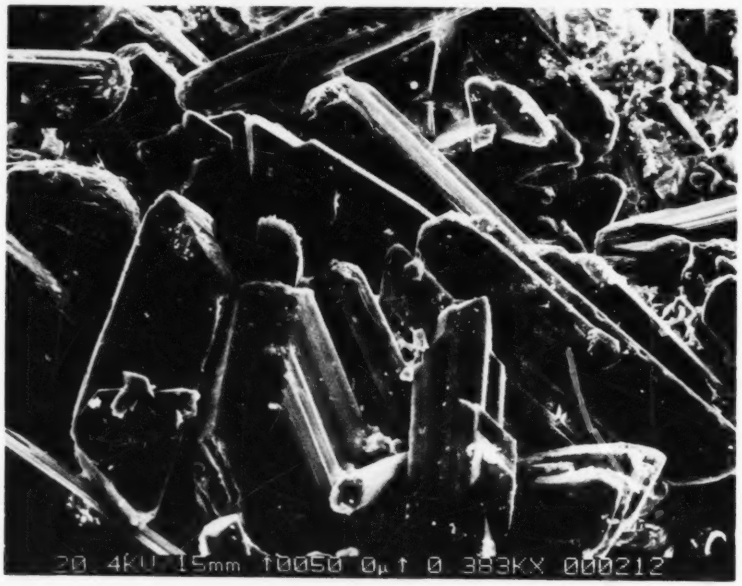
20 4KU 15mm ↑0050 0μ↑ 0 383KX 000212

Figure 6-9. Springfield full-scale solids no. 212.
Solids: 98% oxidation.
Slurry: pH 5.5, no adipic acid additive.

are nearly an order of magnitude larger than those from the bench-scale unit due, in part, to a three-or fourfold difference in the solid residence times.

One of the Springfield solids samples was obtained when the system was experiencing limestone blinding. As mentioned earlier, limestone blinding is most likely caused by surface precipitation of calcium sulfite on the limestone surface. In an effort to directly substantiate this hypothesis, the limestone crystals in this sample were analyzed by x-ray fluoresence spectroscopy. The exciting electron beam diameter is on the order of 70 Å (10^{-4} microns) with a maximum excitation depth of approximately 2 microns. The results are illustrated by Figure 6-10. The spectra of the limestone particle, Figure 6-10 (a), is placed directly above that of a calcium sulfite platelet from a bench-scale sample, Figure 6-10 (b). The greatly reduced sulfur peak intensity in the spectrum from the limestone as compared to the sulfur peak intensity in the calcium sulfite suggest the presence of very little sulfur. A peak of this intensity could result from the presence of sulfur bearing species precipitating on the surface during the drying process. This result fails to either confirm or rule out the proposed limestone blinding hypothesis.

Radian's adipic acid modified equilibrium program was run to measure the differences in relative saturation for the bench-scale tests with increasing liquid phase adipic acid. The relative saturation for calcium sulfite was seen to increase from 5.25 to 8.32 for a corresponding increase in liquid phase adipic acid from 877 ppm to 6780 ppm. This result suggests that adipic acid may indeed effect the relative saturation of calcium sulfite in scrubber liquors. The increase in the relative saturation of calcium sulfite may increase the nucleation rate of calcium sulfite at the expense of crystal growth.

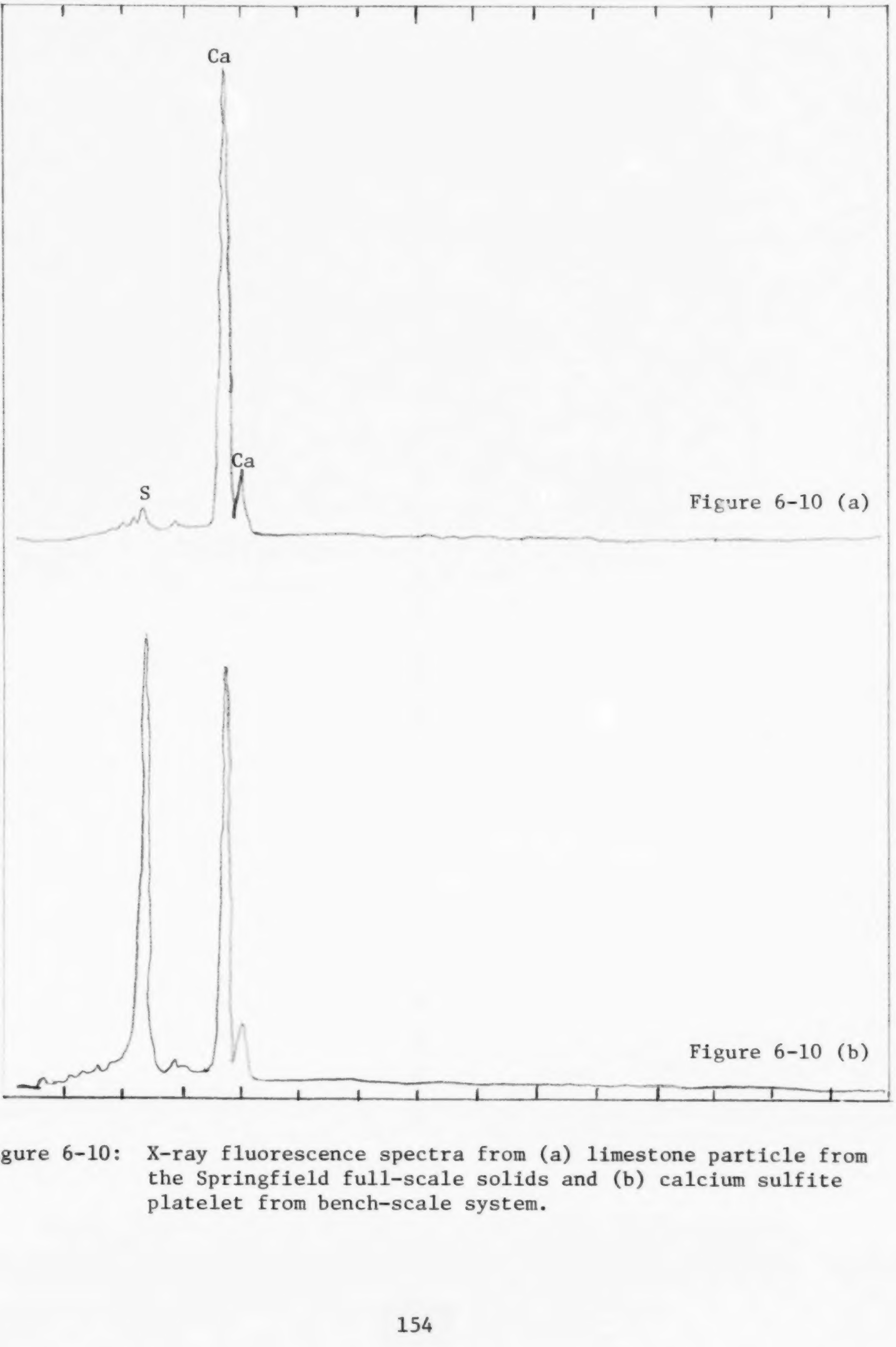

Figure 6-10: X-ray fluorescence spectra from (a) limestone particle from the Springfield full-scale solids and (b) calcium sulfite platelet from bench-scale system.

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APPENDIX A

ANALYTICAL METHODS

A.1.0 OVERVIEW

The measurement of adipic acid and its degradation products were discussed in Section 5. However, numerous other physical tests and chemical analyses were required in order to characterize adipic acid degradation. Table A-1 summarizes these analyses by sample source and phase.

A.2.0 PHYSICAL TESTING

Physical testing consisted mainly of measurements taken during the bench-scale runs to maintain steady state operation. The measurements included:

- hold tank pH,
- hold tank and gas inlet temperature, and
- weight percent solids in the slurry.

Slurry pH was monitored with two independent pH meters. The first meter was corrected to a strip chart recorder to provide a continuous trace of the hold tank pH during the run. The second pH meter was an integral part of a pH controller. The output of the pH controller was used to control the limestone into the hold tank. In most cases, deviations of only 0.05 pH units from the set point could be maintained.

Both the temperature of the hold tank and the inlet flue gas were monitored. The hold tank temperature was maintained within 1°F of the set point. Inlet gas temperature, however, tended to fluctuate due to changes in ambient conditions.

TABLE A.1 SUMMARY OF ANALYSES

Sample Phase	Hold Tank Slurry	Filter Drum Solids	Gas Outlet	Gas Inlet
Liquid	$\left.\begin{array}{l} SO_3^{=} \\ SO_4^{=} \\ Cl^{-} \\ Ad^{=} \\ Deg \end{array}\right\}$ anions $\left.\begin{array}{l} Ca^{++} \\ Mn^{+} \\ Fe^{+++} \\ Na^{+} \end{array}\right\}$ cations[a]	N.A.	(Blowover) $Ad^{=}$ Deg	N.A.
Solid	$SO_3^{=}$ $SO_4^{=}$[a] Cl^{-} $Ad^{=}$ Deg $\left.\begin{array}{l} Ca^{++} \\ Mn^{++} \\ Fe^{+++} \end{array}\right\}$ cations[a] Acid Insoluble Quantity[b]	$SO_3^{=}$ $SO_4^{=}$ Cl^{-} Ad Deg $\left.\begin{array}{l} Ca^{++} \\ Mn^{++} \\ Fe^{+++} \end{array}\right\}$ cations[a] Acid Insoluble Quantity[b]	N.A.	N.A.
Gas	N.A.	N.A.	SO_2 $Ad^{=}$ Deg	SO_2 Temp
Slurry	pH Temp Density	N.A.	N.A.	N.A.

[a] On selected samples only

[b] Limestone and fly ash runs only

N.A. = Not applicable

Deg = Degradation Products

Hold tank slurry density was measured at operating temperatures by weighing a clean preweighed volumetric flask filled to the calibration mark. The contents of the flask were immediately vacuum filtered on a preweighed filter paper. The filtered solids were mixed thoroughly and transferred to three preweighed drying pans. The pans and filter paper were oven dried below 60°C to prevent crystal dehydration. Both the dried solids and the filtrate were saved for chemical analyses.

A.3.0 CHEMICAL ANALYSES

Specific techniques used to analyze gas, liquid, and solid phase samples are presented in this section.

A.3.1 GAS PHASE ANALYSES

Gas phase analyses included the measurement of both the inlet and outlet SO_2 concentration and analysis of the outlet flue gas for hydrocarbons from adipic acid degradation. The analyses for hydrocarbons has been discussed in Section 5.

The inlet and outlet SO_2 concentrations were monitored with a Theta SO_2 analyzer. The Theta SO_2 analyzer uses a conductivity cell to measure the SO_2 concentration. Cooling of the outlet gas stream was required to prevent condensation in the analyzed cell. In field testing, a glass wool filter was used to prevent fly ash from entering the analyzer cell.

A.3.2 LIQUID PHASE ANALYSES

The liquid phase samples from bench-scale testing were analyzed for adipic acid and its degradation products, cations including calcium, manganese, iron, and sodium, and anions including chloride, sulfite, sulfate, and thiosulfate. The analyses of adipic acid and its degradation products was described in Section 5.

Calcium, magnesium, iron, and sodium cations were analyzed by atomic absorption spectroscopy. Atomic absorption involves the aspiration of the liquid into a flame where the cation to be analyzed is reduced to its elemental form and vaporized into the light path of a radiation source characteristic of the species. Within limits, the absorption of the characteristic radiation is linearly dependent upon the concentration of the species present. Thus, the species concentration of a sample is determined by comparing the absorption of the unknown with the absorption of standards of known concentration.

Chloride and sulfate ions were analyzed by ion chromatography (IC). The procedure is similar to that used for the adipic acid analyses. However, a shorter separator column was used since there was no need to resolve the adipic acid peak. This procedure greatly reduced the amount of time required for these analyses. Sulfite and thiosulfate determinations involved iodine titrations.

Case 1: Samples containing sulfite only

Quantitative samples were added to a pH 6 buffered solution containing 10 ml of standardized iodine solution. The excess iodine was back titrated with a standard solution of thiosulfate. All determinations were in duplicate with a minimum of one blank determination per sample set. It is particularly important to allow sufficient time for the sulfite to react with the iodine. Therefore, the solutions were stirred for a minimum of ten minutes before completing the back titration. The endpoint is determined by the disappearance of the blue iodine-starch colloid complex.

Calculations:

Liquid phase

$$\text{mmole } SO_3\text{/liter} = \frac{(B-S)\ N\ (1000)}{2\ V} \qquad \text{(Eq. A-1)}$$

where,

B = ml of iodine standard required for blank,

S = ml of iodine standard required for sample,

N = normality of iodine solution,
V = volume of sample in milliliters, and
M = mass of sample in grams.

Case 2: Samples containing both sulfite and thiosulfate

When both sulfite and thiosulfate were present, two qualitative sample aliquots were analyzed. Aliquots were added to pH 6 buffered solutions. In one portion, only thiosulfate is measured after complexing the sulfite with formaldehyde. The solution was titrated with standard iodine solution to the formation of the blue iodine-starch complex. The second aliquot was analyzed using the method outlined for Case 1; this results in the sum of sulfite and thiosulfate present. Sulfite is then determined by correcting for the thiosulfate present.

Calculations:

$$\text{mmole } S_2O_3/\text{liter} = \frac{I_a \, N \, (1000)}{V_a}$$

$$\text{mmole } SO_3^{=}/\text{liter} = \frac{(B - I_b - S_b) \, N \, (1000)}{2V_b}$$

where,

I_a = ml of iodine titrant required to react with thiosulfate,

I_b = $I_a(V_b/V_a)$, correction for difference in aliquot volumes,

N = normality of iodine standard,

V_a = volume of first aliquot for determination of thiosulfate,

V_b = volume of second aliquot for determination of thiosulfate + sulfite, B = ml of standard thiosulfate required to react with iodine blank, and

S_b = ml of thiosulfate titrant required to react with excess iodine in aliquot B.

A.3.3 SOLID PHASE SAMPLES

Bench-scale solids were analyzed for adipic acid, chloride, sulfite, sulfate, and total sulfur (for determining the percent oxidation), and calcium (used with the total sulfur to determine the limestone utilization).

The analyses for adipic acid, total sulfur, chloride, and sulfate are done by performing a dissolution on the solid sample. These procedures are described below.

Solid Dissolution Procedure for the Adipic Acid Analysis

- Approximately 0.5g of the dry solids to be analyzed were weighed and quantitatively transferred to a clean 250 ml volumetric flask one-half full of deionized water,
- while stirring, add 4ml (or less) of 1N HCl, continue stirring for 15 minutes,
- remove the stir bar, dilute to the calibration mark and mix thoroughly,
- transfer a suitable quantity to a polyethylene sample bottle and store in the refrigerator until analyzed by ion chromatography-exclusion (ICE).

Solid Dissolution Procedure for the Total Sulfur Analysis

- Accurately weigh approximately 0.5g of the dry solids and
- quantitatively transfer the solids to a 250ml volumetric flask one-half full of deionized water,
- add 1ml of 30% H_2O_2 and stir for a minimum of ten minutes,
- add 1 N HCl dropwise until the solids dissolve,
- remove the stir bar, and dilute to the calibration mark, and
- transfer to a sample bottle and save for analysis (sample need not be refrigerated) by ion chromatography (IC).

Solid Dissolution Procedure for the Chloride Analysis

- Quantitatively transfer 0.5g sample to a 250ml volumetric flask one-half full of deionized water,
- add 4ml 1 N HNO_3, stir until dissolution is complete,
- remove the stir bar and dilute to the calibration mark, and
- transfer to a sample bottle and save for analysis (refrigeration is not necessary) by ion chromatography (IC).

Solid Dissolution Procedure for the Sulfate Analysis

- Quantitatively transfer 0.5g sample to an impinger containing approximately 200ml deionized water.
- Add HCl to dissolve the solids. Continue adding HCl until the solution is at pH 1.
- Purge the solution with pure nitrogen until SO_2 is no longer evolved. (This was confirmed by measurement of the SO_2 concentration in the purge stream.)
- Transfer the solution to 250ml volumetric flask and rinse the impinger with additional deionized water.
- Analyze the solution for sulfate by ion chromatography (IC).

The analysis for calcium in the solids was done by atomic absorption spectroscopy using the dissolution for total sulfur. Sulfite in the solids was determined by the same technique as the liquid phase sulfite analysis. No acid was required to dissolve the solids.

A.4.0 QA/QC PROCEDURES

The procedures used to maintain quality assurance and quality control are outlined in this section.

pH - The pH of the hold tank slurry was measured by two independent pH meters. The first was calibrated with pH 4.0 and pH 7.0 standard solutions. The output of this pH meter was recorded using a strip chart recorder. The second pH meter was an integral part of a pH controller. This meter was calibrated against the first pH meter at the desired hold tank pH. The output of the pH controller was used to regulate the flow of limestone into the hold tank. The use of two independent measurements of pH allowed early detection of operating problems involving pH. One such problem was scale formation on the pH electrodes.

Gas Phase SO_2 Concentration - The inlet and outlet SO_2 concentration was measured with a Theta SO_2 analyzer. The analyzer was calibrated with a 3050 ppm SO_2 in N_2 standard before the start of each run.

Slurry Measurements - The volume of slurry in the system was measured by calibrating the hold tank with a volumetric pipette. The calibration was checked and adjusted as necessary when changes in the system affecting the total system volume were made. The slurry density was measured by taking the slurry sample in a preweighed 250 ml volumetric flask. The weight percent solids in the slurry was determined by weighing the filtered solids and then correcting for the moisture in the wet filter cake. The moisture in the filter cake was determined by drying the solids in an oven at temperatures no higher than 60°C. This procedure was performed in triplicate. To prevent oxidation of solids during the drying procedure, the oven was purged with nitrogen.

Ion Chromatography Analysis - Chemical species analyzed by IC include adipic acid, chloride, and sulfate. For the determinations of chloride and sulfate, a three-point calibration curve was generated using solutions of known concentration. The procedure for adipic acid was slightly different. For the determination of adipic acid, the sample was diluted so that the concentration of adipic acid was about 50 ppm. Then, the sample was bracketed by 50 ppm standards during the IC analysis. This procedure was repeated at least two times for each sample.

Ion Chromatography-Exclusion Analyses - An ICE analysis was performed to obtain the solid phase adipic acid concentrations and the concentrations of some adipic acid degradation products. The analysis for adipic acid in the solid phase was performed on ICE using an HCl dissolution of the solid sample. Each sample was bracketed by standard solutions which contained a matrix of chloride and sulfate similar to that of the solid dissolution. The ICE analysis for adipic acid is not as reproducible as the IC analysis. Therefore, solid samples which were found to contain significant quantities of adipic acid were analyzed as many as five times. For the determination of adipic acid degradation products, standards were used which contained known concentrations of several acids of interest. In general, the standard was injected just after the sample to verify the retention times and the response factors of carboxylic acids in the sample.

Gas Chromatography Analyses - Gas chromatography was used to analyze gas phase samples for hydrocarbons and liquid phase samples for mono- and dicarboxylic acids. The concentrations of hydrocarbons in the gas phase were determined by injecting a standard containing known concentrations of C_1-C_6 hydrocarbons. In the determination of liquid phase monocarboxylic acids, a standard solution containing each of the monocarboxylic acids was injected prior to the analysis of the sample. After the analysis of the sample, the sample was spiked with a known amount of the standard solution and re-analyzed. This procedure provided confirmation of peak identity and also gave a double check on the concentration of each of the acids. The procedure for analysis of the dicarboxylic acids was identical to that used for the monocarboxylic acids.

Atomic Absorption Spectroscopy - Atomic absorption spectroscopy was used to analyze for calcium, sodium, iron, and manganese in both liquid and solid phase samples. The concentration of these metals was determined with a three-point calibration curve using standards of known concentration. The calibration curve was verified by analyzing NBS standards.

APPENDIX B

SAMPLE CALCULATIONS

The procedures utilized in calculating the adipic acid degradation rate from the raw data are presented in this appendix. An error analysis is also provided. The calculations shown here are for run R-18.

As described in Section 3.1, the adipic acid degradation rate is determined by mass balance. Part of this mass balance is the determination of the initial and final adipic acid inventories. The raw data used to calculate these inventories is given below.

Acid Analyses

Adipic Acid Liquid Analyses by IC	Initial sample - 2509; 2534; 2518; 2578 Average - 2535 ppm Final sample - 2600; 2653; Average - 2627 ppm (Final sample analyzed ≃1 month later at 2609 ppm.)
Adipic Acid Solids Analyses by ICE (These analyses not yet corrected for liquid associated with the filter cake.)	Initial sample - 747; 745; 978 Average - 823 ppm Final sample - 324; 345 Average - 335 ppm Filter cake - 900; 1021; 951 Average - 957 ppm

Glutaric Acid
Liquid Analyses

ICE - 659; 744; 461
GC - 622
Average - 620 ppm

Slurry Characteristics

	Initial Sample	Final Sample
Density ρ, g/ml (@ 125°F)	1.0098	1.0123
Wt. % solids in hold tank	3.10	3.40
Slurry Volume, ml (@ 125°F)	1995	1995
Wt. % solids in filter cake	76.2; 76.7; 76.2	85.8; 86.8; 87.0
Average	76.4	86.5
Manganese concentration, ppm	5.4	6.2

Mass of dry filter cake solids = 398.6 g

% oxidation of all solids = 100%

Run R-18 was done with manganese. As reported in Section 3.3.2, glutaric acid was formed as a primary degradation product. Glutaric acid coelutes with adipic acid by IC. Therefore, the adipic acid concentration obtained by IC included glutaric acid and must be adjusted accordingly. The glutaric acid found in the final sample is assumed to have been produced at a constant rate over the length of the run including the four hour line-out period. The estimated concentration of glutaric acid in the inital sample is then:

$$620 \text{ ppm glutaric acid} \left(\frac{4 \text{ hours}}{4+22 \text{ hours}}\right) = 95 \text{ ppm glutaric acid}$$

The response factor for glutaric acid by IC is 1.46 times that of acipic acid.

If $(X)_L$ = liquid phase IC analysis for acipid acid, and $(Glu)_L$ = liquid phase concentration of glutaric acid, then the actual liquid phase concentration of adipic acid $(Ad)_L$ is:

$$(Ad)_L = (X)_L - 1.46(Glu)_L$$

For the initial sample:

$$\begin{aligned}(Ad)_L &= 2535 - 1.46(95) \\ &= 2396 \text{ ppm adipic acid}\end{aligned}$$

For the final sample:

$$\begin{aligned}(Ad)_L &= 2627 - 1.46\ (620) \\ &= 1722 \text{ ppm adipic acid}\end{aligned}$$

Note that the concentration of adipic acid could have been determined directly. However, the nature of the ICE method is such that the above adjustment procedure was judged to give the best overall accuracy. This procedure was used to adjust the IC adipic acid analyses for all runs in which greater than 50 ppm glutaric acid was found in the final sample.

From the slurry data, the total mass, the mass of liquid, and the mass of solids in the hold tank can be calculated:

$$\text{Total mass, } M_T = (\text{density, } \rho)(\text{slurry volume, } V_S)$$

$$M_T = \rho V_S$$

$$\text{Mass of dry solids, } M_S = \frac{\left(\text{density, } \rho\right)\left(\text{slurry volume, } V_S\right)\left(\begin{matrix}\text{Wt. \% solid in} \\ \text{hold tank, } S\end{matrix}\right)}{100}$$

$$M_S = \rho V_S S/100$$

$$\text{Mass of liquid, } M_L = (\text{total mass, } M_T) - (\text{mass of solids, } M_S) = M_T - M_S$$

The results for R-18 are:

	Initial Sample	Final Sample
Total slurry mass, M_T	2015 g	2020 g
Mass of liquid, M_L	1952 g	1951 g
Mass of dry solids, M_S	62.5 g	68.7 g

We now have the total mass of liquid, the liquid phase adipic acid concentration, and the mass of dry solids. To obtain the concentration of adipic acid in the dry solids, the adipic acid analysis of the solids by ICE must be corrected for the adipic acid in the liquid associated with the filter cake.

The total mass of adipic acid in a solid sample is the sum of the adipic acid in the liquid phase associated with the solids before drying and the adipic acid coprecipitated in the solids themselves:

$$\begin{array}{c}\text{Total mass of adipic}\\ \text{acid in a solid sample}\end{array} = \begin{array}{c}\text{Mass of adipic acid}\\ \text{contributed by liquid}\\ \text{in the filter cake}\end{array} + \begin{array}{c}\text{Mass of adipic acid}\\ \text{coprecipitated in}\\ \text{the solid phase}\end{array}$$

The components of this mass balance can be solved in terms of run variables:

$$\begin{array}{c}\text{Total mass of adipic acid}\\ \text{in a solid sample}\end{array} = (\text{mass of dry solids})\ \frac{\text{ICE solids analysis}}{10^6}$$

$$\begin{array}{c}\text{Mass of adipic acid}\\ \text{contributed by liquid}\\ \text{in the filter cake}\end{array} = (\text{mass of wet solids})\left(\frac{100 - \begin{array}{c}\text{Wt.\% solids}\\ \text{in filter}\\ \text{cake, C}\end{array}}{100}\right)\left(\frac{\begin{array}{c}\text{Adipic acid conc.}\\ \text{liquid, } (Ad)_L\end{array}}{10^6}\right)$$

$$= \frac{\text{mass of dry solids}}{(C/100)}\quad \frac{(100-C)}{100}\quad \frac{(Ad)_L}{10^6}$$

$$= \text{(mass of dry solids)} \left(\frac{\text{Ad}_L}{10^6}\right)\left(\frac{100}{C} - 1\right)$$

$$\begin{array}{c}\text{Mass of adipic acid} \\ \text{coprecipitated in the} \\ \text{solid phase}\end{array} = \text{(mass of dry solids)}\left(\frac{\begin{array}{c}\text{Concentration of adipic acid} \\ \text{in the solids, } (\text{Ad})_S\text{, ppm}\end{array}}{10^6}\right)$$

$$= \text{(mass of dry solids)} \left(\frac{(\text{Ad})_S}{10^6}\right)$$

The solids mass balance then becomes:

$$\left(\cancel{\begin{array}{c}\text{mass of} \\ \text{dry solids}\end{array}}\right)\left(\frac{\begin{array}{c}\text{ICE solids} \\ \text{analysis}\end{array}}{\cancel{10^6}}\right) = \left(\cancel{\begin{array}{c}\text{mass of} \\ \text{dry solids}\end{array}}\right)\frac{(\text{Ad})_L}{\cancel{10^6}}\left(\frac{100}{C} - 1\right) + \left(\cancel{\begin{array}{c}\text{mass of} \\ \text{dry solids}\end{array}}\right)\frac{(\text{Ad})_S}{\cancel{10^6}}$$

or: $(\text{Ad})_S = \text{(ICE solids analysis)} - (\text{Ad})_L \left(\frac{100}{C} - 1\right)$

where $(\text{Ad})_S$ represents the actual concentration of coprecipitated adipic acid in the solids phase.

For run R-18, the concentration of adipic acid in the initial solids is:

$$(\text{Ad})_S = 823 - (2396)\left(\frac{100}{76.4} - 1\right)$$

$$= 83 \text{ ppm}$$

and for the final sample:

$$(\text{Ad})_S = 335 - (1722)\left(\frac{100}{86.5} - 1\right)$$

$$= 66 \text{ ppm}$$

These results show that the concentration of coprecipitated adipic acid is quite low. This is typical of well oxidized solids. Note that the amount of coprecipitated adipic acid cannot be determined for the filter cake solids because the concentration of the liquid associated with the filter cake, which varies over the length of the run, is unknown.

The initial and final adipic acid inventories can now be calculated:

$$\text{Adipic Acid Inventory, g} = \frac{M_L(\text{Ad})_L}{10^6} + \frac{M_S(\text{Ad})_S}{10^6}$$

For run R-18, the initial inventory of adipic acid is:

$$\text{Initial Inventory, g} = \frac{(1952)(2396)}{10^6} + \frac{(62.5)(83)}{10^6}$$

$$= 4.682 \text{ g adipic acid}$$

and for the final inventory:

$$\text{Final inventory, g} = \frac{(1951)(1722)}{10^6} + \frac{(68.7)(66)}{10^6}$$

$$= 3.364 \text{ g adipic acid}$$

To calculate the adipic acid degradation rate, several additional components of the mass balance are required. These include the total amount of adipic acid in the solids removed in the filter drum over the course of the run, the mass of makeup adipic acid added semi-continuously over the course of the run, and the mass of any adipic acid lost through entrainment in the flue gas. For run R-18, these components are:

$$\begin{array}{r}\text{mass of adipic acid in}\\ \text{the solids removed in}\\ \text{the filter drum, g}\end{array} = (\text{mass of dry solids})\left(\frac{\begin{array}{c}\text{ICE solids analysis of}\\ \text{the filter drum solids}\end{array}}{10^6}\right)$$

$$= (398.6\text{ g dry solids})\left(\frac{957\text{ ppm}}{10^6}\right)$$

$$= 0.381\text{ g adipic acid}$$

2.200 g of adipic acid was added in run R-18 as a 10,000 ppm stock solution by volumetric burette. The makeup adipic acid was added to the hold tank in even increments each half-hour.

The adipic acid lost through entrainment in the flue gas is recovered in an impinger downstream from the scrubber. In R-18, 400 ml of condensate was recovered with a concentration of 6.3 ppm adipic acid. The total mass of adipic acid in the condensate was:

$$(400)\ \frac{6.3}{10^6} = 0.003\text{ g of adipic acid}$$

The loss of adipic acid by this mechanism was generally very small.

The adipic acid degradation rate can now be calculated from its components:

Initial inventory	4.682 g
- Final inventory	3.364 g
+ Makeup	2.200 g
- Loss in filter drum solids	0.381 g
- loss through entrainment	0.003 g
= Loss through degradation	3.134 g

For run R-18, the total time on gas was 21.7 hours and the total amount of SO_2 removed was 155.1 g.

From these results, the following forms of the adipic acid degradation rate can be computed:

$$\text{Absolute degradation rate} = \frac{\text{total degraded adipic acid}}{\text{total run time}}$$

$$= \frac{3.134}{21.7} = 0.144 \text{ g/hr} \pm 5.5\%$$

$$\text{Normalized degradation rate} = \frac{\text{total degraded adipic acid}}{\text{total } SO_2 \text{ removed}}$$

$$= \frac{3.134}{155.1}(1000) = 20.2 \, \frac{\text{mg adipic acid degraded}}{\text{g } SO_2 \text{ removed}}$$

$$\text{Degradation rate constant, } K_d = \frac{(\text{normalized degradation rate})(6400)}{(\%\text{ solids oxidation})(\text{average adipic acid conc.})}$$

$$= \frac{(20.2)(6400)}{(100)\,\frac{2396 + 1722}{2}}$$

$$= 0.628 \text{ M}^{-1}$$

A propagation of errors analysis has been performed on the method used to calculate the absolute degradation rate. The results of this procedure have been simplified somewhat because calculating an exact experimental uncertainty for each of the bench-scale runs would be an extremely tedious task. The largest source of uncertainty in the calculation of the initial and final adipic acid inventories is in the determination of the liquid phase adipic acid concentration. The results of the error analysis show that for an assumed uncertainty of ±2% in the average of replicate IC analyses, the resulting uncertainty in the inventory is approximately ±3%. The uncertainty in replicate ICE solids analyses was about ±4% and this was the uncertainty attached to the mass of adipic acid in the filter drum solids. The mass of makeup adipic acid added during the run was essentially errorless and the error associated with the small amount of entrained adipic acid was considered negligible. In summary:

Quantity	Uncertainty
Initial inventory	±3%
Final inventory	±3%
Make-up	±0%
Loss in filter drum solids	±4%
Loss through entrainment	negligible

A standard statistical error analysis was used to calculate a 95% confidence interval around the absolute degradation using the above uncertainties. And, these are the uncertainties reported in Table 3-5.

This analysis should provide reasonable estimates of the uncertainty in the absolute adipic acid degradation rate for most of the bench-scale runs. However, the error analysis does not allow for the additional uncertainty in the adipic acid concentration resulting from the correction of the IC results for glutaric acid. The runs for which this correction was made include all runs with manganese and runs R-13, R-19, and R-26. The stated uncertainties for these runs will be somewhat low.